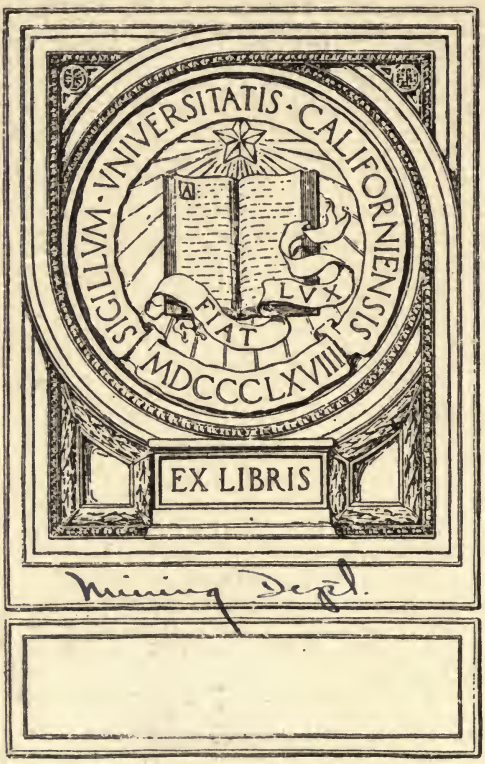
SIGILLVM · VNIVERSITATIS · CALIFORNIENSIS
LVX
FIAT
MDCCCLXVIII
EX LIBRIS
Mining Dept.

THE CHEMISTRY OF CYANIDE SOLUTIONS

Published by the

McGraw-Hill Book Company

New York

Successors to the Book Departments of the

McGraw Publishing Company — Hill Publishing Company

Publishers of Books for

Electrical World
The Engineering Record
Electric Railway Journal
The Engineering and Mining Journal
Power and The Engineer
American Machinist

THE CHEMISTRY OF CYANIDE SOLUTIONS

RESULTING FROM THE TREATMENT OF ORES

By

J. E. CLENNELL, B.Sc. (LOND.)

ASSOCIATE OF THE INSTITUTION OF MINING AND METALLURGY

ASSOCIATE OF THE CHEMICAL, METALLURGICAL, AND MINING SOCIETY OF SOUTH AFRICA

Author of *"Analytical Work in Connection with the Cyanide Process"*

SECOND EDITION

CORRECTED AND ENLARGED

Digitized by Google

NEW YORK

McGRAW-HILL BOOK COMPANY

239 WEST 39TH STREET

1910

TN767
C59
1910

MINING DEPT.

COPYRIGHT, 1904
BY
THE ENGINEERING AND MINING JOURNAL

COPYRIGHT, 1910
BY THE
McGRAW-HILL BOOK COMPANY

UNIV. OF
CALIFORNIA

CONTENTS.

	PAGE
INTRODUCTORY	1
INGREDIENTS OF CYANIDE SOLUTIONS THAT ARE ESTIMATED	2
ACTIVE CYANOGEN COMPOUNDS	4
Free Cyanide	4
Total Cyanide	33
Total Cyanogen	47
Hydrocyanic Acid	52
Available Cyanide	54
ALKALINE CONSTITUENTS	58
Total Alkali	62
Protective Alkali	63
Hydrates, Carbonates and Bicarbonates	66
Ammonia	68
REDUCING AGENTS	70
Reducing Power	70
Ferrocyanides	73
Thiocyanates	87
Sulphides	90
Other Reducing Agents	93
AUXILIARY AGENTS	95
Oxygen	95
Active Haloids	100
Peroxides	101
Ferricyanides	102
INACTIVE BODIES	104
Cyanates and Isocyanates	108
Chlorides	112
Nitrates	112
Sulphates	112
Silicates	113

PAGE

NOBLE METALS 114
Gold and Silver Together 114
Gold Alone 118
Silver Alone 120
BASE METALS 123
Zinc 123
Copper 123
Iron, Alkaline Earths and Alkali Metals 137
SUSPENDED MATTER 138
Total Solids in Suspension 138
Various Constituents in Suspended Matter 140
Total Solids in Solution 141
AN EXAMINATION OF VARIOUS METHODS FOR THE ESTIMATION OF FERROCYANIDE 143
APPENDICES 161–198

UNIV. OF CALIFORNIA

INTRODUCTORY.

In preparing the following treatise, my object has been not so much to give the results of any special researches on individual obscure points as to present a comprehensive and, so far as possible, complete review of the entire subject. For this purpose a short description of well-known methods is introduced, and, where necessary, a critical discussion of their value. I have also described the various modifications of existing methods that have been suggested from time to time, but which have not hitherto been collected and compared, and have given the results of experiments made to test the accuracy of the assumptions on which such modifications are based. While, for the sake of completeness and the clear presentation of the subject, it has been necessary to include much that is already familiar, it is hoped that the points discussed are shown to be of sufficient interest and importance to justify a somewhat extended investigation.

A systematic study of the solutions resulting from the continued working of the cyanide process on some particular class of ore may throw much light on the chemical and economic problems involved in the treatment, and in some instances has proved of great practical value. It is highly desirable, therefore, to have a fairly simple, rapid and reliable system of laboratory tests for determining the amount of any of the more important constituents of such solutions. In addition to these laboratory methods, one or two rough tests are needed which will suffice for controlling the daily routine operations of the plant; such tests should give a clear and unmistakable indication, and should represent some factor of real value in the treatment, though strict scientific accuracy is not a necessity in this case.

NOTE.—The author, owing to absence on professional work, was unable to revise his proofs. The revision was done by Mr. H. E. Bowles, F.I.C., to whom acknowledgment is due by the publishers for this courtesy.

INGREDIENTS OF CYANIDE SOLUTIONS THAT ARE ESTIMATED.

For the purpose of analysis, the various constitutents of a cyanide solution, after use in the treatment of ores, may be conveniently classified as follows:—

Class I.—Active Cyanogen Compounds.
Class II.—Alkaline Constituents.
Class III.—Reducing Agents.
Class IV.—Auxiliary Agents.
Class V.—Inactive Bodies.
Class VI.—Noble Metals.
Class VII.—Base Metals.
Class VIII.—Suspended Matter.

The estimations which will be considered under each of these heads are here summarized.

Class I.—Active Cyanogen Compounds.

1. Free cyanide.
2. Total cyanide.
3. Total cyanogen.
4. Hydrocyanic acid.
5. 'Available' cyanide.

Class II.—Alkaline Constituents.

1. Total alkali.
2. 'Protective' alkali.
3. Alkaline hydrates.
4. Alkaline carbonates and bicarbonates.
5. Ammonia and ammonium salts.

Class III.—Reducing Agents.

1. Reducing power.
2. Ferrocyanides.
3. Thiocyanates.
4. Organic matter.
5. Sulphides.
6. Nitrites.

Class IV.—Auxiliary Agents.

1. Oxygen.
2. Active haloids.
3. Peroxides.
4. Ferricyanides.

Class V.—Inactive Bodies.

1. Cyanates and isocyanates.
2. Chlorides.
3. Nitrates.
4. Sulphates.
5. Silicates.

Class VI.—Noble Metals.

1. Gold and silver together.
2. Gold alone.
3. Silver alone.

Class VII.—Base Metals.

1. Zinc.
2. Copper.
3. Iron.
4. Alkaline earths.
5. Alkali metals.

Class VIII.—Insoluble (Suspended) Matter.
(*Organic and Inorganic.*)

In exceptional cases some accidental impurities not included in the above list may have to be estimated. Thus organic matter has been supposed to exist in these solutions in a variety of forms, some of considerable complexity, but as a rule no useful object would be served by special estimations of these bodies, *e. g.*, formates, oxamide, urea, etc., and they will not be considered in the present discussion.

CLASS I.

ACTIVE CYANOGEN COMPOUNDS.

Under this head will be considered those cyanogen compounds which are of more or less practical value as solvents for the precious metals. Some of the cyanogen compounds included in the estimations of 'total cyanide' and 'total cyanogen,' however, are not solvents of gold and silver.

SECTION 1.

Estimation of Free Cyanide.

The term 'free cyanide' will be used to indicate the equivalent, in terms of potassium cyanide, of all the cyanogen which is present in the solution as simple cyanides of the alkalis and alkaline earth metals, such as KCy, NaCy, NH_4Cy, $CaCy_2$ and $BaCy_2$. It does not include cyanogen present in the form of double cyanides or hydrocyanic acid.

Methods.

The principal methods hitherto proposed for estimating free cyanide are as follows:

1. The silver nitrate method, proposed in its original form by Liebig.
2. The iodine method, generally ascribed to Fordos and Gélis.
3. The mercuric chloride method of Hannay.
4. The cuprammonium method. (Buignet.)

Method No. 1.

Estimation of Free Cyanide by Titration with Silver Nitrate.

(*A*) *Liebig's Method* (*Unmodified*).

This method, either in its original form or with certain modifications to be discussed later, is the one almost universally adopted in the actual daily tests made for regulating the strength of solutions in use for the treatment of ores.

The process depends upon the fact that when a solution of nitrate of silver is added drop by drop to a liquid containing simple cyanides of the alkali or alkaline earth metals, each drop of the solution forms a white cloud of silver cyanide. So long as the free cyanide is in excess, this cloud disappears on agitation, forming a soluble double cyanide of silver by combination with the simple cyanide present. The reactions in the case of potassium cyanide are as follows:

$$(a)\quad AgNO_3 + KCy = AgCy + KNO_3.$$
$$(b)\quad AgCy + KCy = KAgCy_2.$$

The completion of the reaction is shown by the permanence of a white turbidity or opalescence. When this point is reached the whole of the free cyanide has been converted into a double salt of silver, and any further addition of silver nitrate will cause a precipitate of silver cyanide which does not redissolve; thus:

$$(c)\quad AgNO_3 + KAgCy_2 = 2AgCy + KNO_3.$$

It will be noted from these reactions that one molecule of silver nitrate is equivalent to two molecules of potassium cyanide, the complete series of reactions up to the point where a permanent turbidity appears being expressible in one equation, as follows:

$$(d)\quad AgNO_3 + 2KCy = KAgCy_2 + KNO_3.$$

[Hence 169.89 parts of $AgNO_3$ are equivalent to 130.22 parts of KCy, or 1.3046 parts $AgNO_3$ = 1 part of KCy.]

Standard Solutions. — The solution most commonly used in testing by this method is prepared by dissolving 13.0464 grams of pure crystallized nitrate of silver in distilled water, and diluting until the whole volume of the solution is 1,000 c.c. Every c.c. of this solution is equivalent to 0.01 gram KCy. Hence if we take 10 c.c. of the cyanide solution which is to be tested, every c.c. of the silver solution added will represent 0.1 per cent. of 'free cyanide.'

For testing dilute solutions, it will be more convenient to prepare a standard silver nitrate solution of half this strength, *i.e.*, containing 6.5232 grams of silver nitrate dissolved to a liter. Every c.c. of this solution is equivalent to 0.005 gram KCy; hence if we take 50 c.c. (a convenient quantity for dilute solutions) of the liquid to be tested, every c.c. of the standard $AgNO_3$ added will represent 0.01 per cent. KCy.

If a decinormal solution of silver nitrate, however, be used,

1 c.c. = 0.013022 gram KCy; hence if we take 13 c.c. of the liquid to be tested, 1 c.c. N/10 $AgNO_3$=0.1 per cent free cyanide.

Mode of Carrying Out the Test.—A measured volume (varying, according to the strength of the solution to be tested, from 5 to 100 c.c.) is taken by means of a measuring column or pipette, and transferred to a small flask or beaker, a small conical Erlenmeyer flask being very suitable for the titration. The silver nitrate solution is now run in from a burette. If the strength of cyanide is approximately known, the standard solution may be added rapidly at first, finishing drop by drop. The flask should be placed in a good light and the reaction observed against a dark background. The foot of the burette-stand may be painted a dull black or well rubbed with charcoal. It is sometimes found convenient to have the burette-stand raised until the flask containing the solution to be tested is about on a level with the eye, so that the finishing point may be conveniently observed by looking through the liquid. With pure solutions no difficulty will be found in observing the exact point at which the solution in the flask becomes permanently turbid.

Very strong solutions, such as contain 1 per cent KCy or over, should be diluted with distilled water before testing, as otherwise the silver cyanide may be precipitated in a granular form which dissolves with difficulty in the excess of cyanide. (In some cases this granular precipitate seems to consist wholly or partially of carbonate of silver.) Any difficulty in observing the finishing point due to this cause may generally be obviated by the use of the alkaline iodide indicator to be described below.

Solid Cyanide.—In testing samples of solid cyanide a certain quantity (say 1 to 5 grams) is weighed out exactly in a stoppered bottle, or weighing tube, and dissolved in a large quantity of distilled water. The solution is then made up to a definite volume, say, a liter, and after thorough mixing, a measured portion (50 or 100 c.c.) is tested, as above described, with standard silver nitrate solution. In this connection it is well to bear in mind that what is determined by this and other methods of estimating free cyanide is not actually the potassium cyanide, but the cyanogen, which may in reality be present as a sodium, calcium, ammonium or other salt. This cyanogen being reported as its equivalent in potassium cyanide, a sample of pure cyanide of sodium would appear to contain over 132 per cent KCy.

Turbid Solutions.—When the solutions are at all turbid, they must be filtered, as the end-point cannot be observed with any approach to accuracy unless the liquid be perfectly clear. Solutions occurring in ore treatment sometimes contain very finely divided matter in suspension, which will pass through all ordinary filter papers, and cannot be removed even by repeated filtration. In such cases the liquid may generally be clarified, however, by the addition of lime, which causes a flocculation and settlement of the suspended matter, and allows the liquid to be filtered perfectly clear. With solutions free from zinc, and otherwise comparatively pure, the use of lime for this purpose is admissible, but it is necessary, after lime has been used for the above purpose, to add the potassium iodide indicator described below, when a perfectly correct titration of the free cyanide is required. When zinc is present, the addition of lime is inadmissible; the effect produced will be discussed later under 'Estimation of Total Cyanide.'

Influence of Foreign Salts on Liebig's Method.

The method above detailed works admirably with pure cyanide solutions, but gives very uncertain and inaccurate results in presence of some of the impurities which are generally introduced during treatment of ores.

Zinc occurs chiefly as double cyanide of zinc and potassium, perhaps also as a soluble double ferrocyanide of the same metals. The finishing point is almost always obscure and indefinite, and is, moreover, affected by a variety of circumstances, which will be discussed in detail later on.

Alkalis (hydrates, carbonates and ammonium salts) cause slight errors, the apparent strength being generally in excess of the truth. With free ammonia the error is considerable.

Ferrocyanides, thiocyanates and *chlorides* slightly interfere, also rendering the results too high, but the error is scarcely appreciable unless excessive quantities are present.

Thiosulphates (hyposulphites) render the titration quite erroneous, as they readily dissolve the cyanide of silver, so that the results appear much higher than the truth.

Sulphides give an immediate black or brown coloration, which obscures and entirely vitiates the result of the titration with silver. The method of procedure when sulphides are present will be detailed later.

(A_1) *Liebig's Method with Sodium Chloride as Indicator.*

In Liebig's original paper (*Ann. der Chem. u. Pharm.*, 77, 102) the addition of sodium chloride is recommended as an indicator, apparently on the assumption that a precipitate of silver chloride will occur immediately on adding a drop of silver nitrate in excess of the amount required to convert all the cyanide into $KAgCy_2$ (or an equivalent compound). It has been shown, however, by G. Denigès (*Ann. de Chim. et de Pharm.*, Series 7, Vol. VI., p. 381) that chlorides cannot be precipitated by silver salts in presence of cyanides such as KCy, etc., until after the complete precipitation of the cyanides as AgCy. Since the same reactions take place whether sodium chloride be present or not, it is evidently of no value as an indicator.

(*B*) *Liebig's Method with the Potassium Iodide Indicator.*

Neutral Iodide Indicator.

The use of potassium iodide as an indicator for the finishing point of the reaction in Liebig's method is stated to have been suggested originally by J. S. McArthur, and depends on the following considerations:

(*a*) Iodide of silver is readily dissolved by free alkaline cyanides.

(*b*) Iodide of silver is almost absolutely insoluble in solutions of alkaline hydrates, monocarbonates and ammonium salts, and also in free ammonia, which latter dissolves cyanide and chloride of silver easily.

(*c*) In a mixture containing cyanides, chlorides and iodides in solution, the iodide will be precipitated in preference to the cyanide, and the cyanide in preference to the chloride, on addition of silver nitrate.

(*d*) The presence of a small trace of iodide of silver imparts a yellowish tinge to the precipitate, which makes the exact finishing point somewhat more distinct.

When the iodide indicator is used, the successive reactions occurring on addition of silver nitrate appear to be as follows:

Momentary formation of silver iodide, where $AgNO_3$ is locally in excess,

$$(a)\quad AgNO_3 + KI = AgI + KNO_3.$$

This dissolves on agitation, so long as the liquid contains an excess of cyanide:

$$(b)\ AgI + 2KCy = KI + KAgCy_2.$$

Precipitation of silver iodide, when no more free cyanide is present, the precipitate remaining permanent on agitation, and showing a faint yellow tinge:

$$(c)\ AgNO_3 + KI = AgI + KNO_3.$$

This latter reaction occurs in preference to the reaction

$$AgNO_3 + KAgCy_2 = 2AgCy + KNO_3$$

so long as potassium iodide is present.

G. Denigès (*Ann. de Chim. et de Pharm.*, Series 7, Vol. VI., p. 381) describes the following experiment, which throws considerable light on the reactions of silver with cyanides and haloid salts:

Twenty c.c. of 1 per cent potassium cyanide were taken in each case and mixed with

(*a*) 0.5 gram sodium chloride.

(*b*) 0.5 gram potassium bromide.

(*c*) 0.5 gram potassium iodide.

Sufficient silver nitrate was added to each to give a slight precipitate. This was dissolved by 1 c.c. of the cyanide solution, and then silver nitrate solution again added in quantity equal to that originally used. The precipitate, after washing, was examined in each case, and showed the following composition:

(*a*) Exclusively silver cyanide.

(*b*) Silver cyanide with a very little silver bromide.

(*c*) Exclusively silver iodide.

It will be seen that the use of this indicator corrects any error that might arise from the presence of alkali or ammonia. It will also be evident that chlorides or bromides would be useless as indicators.

The test is generally made by adding a few drops of a strong (say 10 per cent) solution of potassium iodide to the liquid which is to be titrated. I have generally found it more convenient to add to each test from 5 to 10 c.c. of a neutral 1 per cent solution of potassium iodide.

Correction of Errors.—Any errors introduced in the titration as made without indicator, owing to the presence of alkalis, ammonia, ammonium salts, chlorides, ferrocyanides or thiocyanates, are more or less corrected by the addition of iodide indicator. (See tables of results.)

Titration in Presence of Zinc.—In solutions containing little or no free alkali, a whitish turbidity ($ZnCy_2$) forms at a certain stage, and increases on addition of more $AgNO_3$. The yellow precipitate of AgI, momentarily formed, is dissolved on agitation until a further point is reached, at which a faint yellow tint becomes permanent. In exactly neutralized solutions (*i.e.*, solutions containing no alkaline hydrates or monocarbonates), the first appearance of a distinct whitish turbidity indicates the free cyanide. [In strongly alkaline solutions the white precipitate either does not remain permanent on agitation or only forms towards the end of the titration, and the final yellow tint indicates the so-called total cyanide, *i.e.*, the equivalent, in terms of KCy, of the cyanogen present as simple cyanides, together with that as K_2ZnCy_4. This matter will be fully treated under 'total cyanide.'] The method of obtaining an exactly neutralized solution will be given in discussing the determination of 'protective alkali.'

Titration in Presence of Copper.—When the solution contains a double cyanide of copper and an alkali metal, the indication obtained with the iodide indicator is much lower than without it. The number obtained with the iodide appears to correspond with the actual free cyanide present. Without the indicator a portion of the cyanogen of the double salt is also determined. This case may also be more conveniently treated under 'total cyanide.'

Alkaline Iodide Indicator.—The addition of a strong solution of caustic potash or soda, together with potassium iodide, has been in general use for some time past for estimating 'total cyanide' and appears to have been independently suggested by Bettel and Goyder in 1895. The reactions will be discussed under 'total cyanide.'

G. Denigès in 1893 published a method of estimating silver by adding an excess of standard potassium cyanide, and determining the excess by titrating with N/10 silver nitrate, with addition of ammonia and potassium iodide, until a faint cloud of silver iodide is formed. In a further investigation published in 1897 (*Ann. de Chim. et de Pharm.*, Series 7, Vol. VI., p. 381), he recommends this method for the estimation of cyanogen, stating that the finishing point is much sharper than that obtained in Liebig's original process, or even than that obtained by the use of neutral potassium iodide as indicator. The granular precipitate sometimes observed in titrating cyanide solutions, especially towards the finish, does not occur, or is rapidly redissolved in presence of ammonia.

W. J. Sharwood (*Journal,* Amer. Chem. Soc., 1897, p. 400) gives a detailed account of the application of this process in the titration of impure solutions, and recommends as indicator 5 c.c. of commercial ammonia with 2 c.c. of 5 per cent potassium iodide, to be added to each test, taking 25 to 100 c.c. of the cyanide solution to be examined. For smaller quantities of cyanide solution he uses 1 c.c. each of ammonia and iodide. The indicator may, of course, be made up in a single solution.

I generally use an indicator made by dissolving 10 grams of potassium iodide in 500 c.c. of ordinary ammonia solution, and diluting to 1,000 c.c. For each test 5 to 10 c.c. of this indicator are added to 50 c.c. of the liquid to be titrated.

In presence of zinc this method serves practically for the determination of 'total cyanide.' Sharwood states, however, that the ammoniacal iodide indicator always gives somewhat low results in the titration of solutions containing K_2ZnCy_4, unless caustic alkali be added as well.

The alkali or ammoniacal iodide indicators also correct any errors due to ferrocyanides, sulphocyanides, chlorides, hydrates and ammonium salts. The error introduced by the presence of thiosulphates is much diminished, but does not appear to be entirely eliminated. The extent of these errors, and the use of the indicator in correcting them is clearly shown in the following tables.

Tests Illustrating the Influence of Alkalis on the Titration of Cyanide with Silver Nitrate, and Correction of the Error by Potassium Iodide Indicator.

No. 1.—Hydrates.

Solutions used.

(*a*) Pure cyanide, 0.47% KCy, containing alkali equivalent to 0.006% NaOH.

(*b*) Sodium hydrate, alkalinity to phenol phthaleïn equivalent to 3.84% NaOH.

(*c*) Potassium iodide (neutral), 1% KI.

(*d*) Silver nitrate, 0.652% $AgNO_3$. 1 c.c. = 0.005 gram KCy.

Details of Test.

Volume of cyanide solution (*a*) in each titration = 10 c.c.
Weight of cyanide in portion tested = 0.047 gram.

	Volume of NaOH sol. (*b*) added. c.c.	Volume of KI sol. (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of NaOH in portion tested. Grams.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %
Without iodide.	.....	.....	9.40	0.0006	0.0470	0.470
	5	.....	9.55	0.1926	0.0477	0.477
	10	.....	9.90	0.3846	0.0495	0.495
	15	.....	10.10	0.5766	0.0505	0.505
	25	.....	10.35	0.9606	0.0517	0.517
With iodide.	.....	1	9.40	0.0006	0.0470	0.470
	15	1	9.40	0.5766	0.0470	0.470
	25	3	9.50	0.9606	0.0475	0.475
	25	5	9.40	0.9606	0.0470	0.470

No. 2.—Ammonia.

Solutions used.

(*a*) Pure cyanide, 0.47% KCy, containing alkali equivalent to 0.006% NaOH.

(*b*) Ammonia, 10% of strong solution; 10 c.c. of solution (*b*) required 155 c.c N/10 acid with methyl orange, indicating 2.635% NH_3.

(*c*) Potassium iodide (neutral), 1% KI.

(*d*) Silver nitrate, 0.652% $AgNO_3$; 1 c.c. = 0.005 gram KCy.

Details of Test.

Volume of cyanide solution (*a*) in each titration = 10 c.c.
Weight of cyanide in portion tested = 0.047 gram.

	Volume of NH_3 sol. (*b*) added. c.c.	Volume of KI sol. (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of NH_3 in portion tested. Grams.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %
Without iodide.	.....	.....	9.40	.....	0.0470	0.470
	1	.....	10.30	0.026	0.0515	0.515
	5	.....	14.80	0.132	0.0740	0.740
	10	.....	over 40	0.263	?	?
With iodide.	.....	1	9.40	.....	0.0470	0.470
	10	1	9.50	0.263	0.0475	0.475
	10	3	9.35	0.263	0.0467	0.467
	25	5	9.45	0.659	0.0472	0.472

The error (in absence of iodide) is thus seen to be much more serious with ammonia than with sodium hydrate.

No. 3.—Sodium Carbonate.

Solutions used.

(*a*) Pure cyanide, 0.465% KCy.
(*b*) Sodium carbonate, 10% (from anhydrous Na_2CO_3).
(*c*) Potassium iodide (neutral), 1% KI.
(*d*) Silver nitrate, 0.652% $AgNO_3$; 1 c.c. = 0.005 gram KCy.

Details of Test.

Volume of cyanide solution (*a*) in each titration = 10 c.c.
Weight of cyanide in portion tested = 0.0465 gram.

	Volume of Na_2CO_3 sol. (*b*) added. c.c.	Volume of KI sol. (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of Na_2CO_3 in portion tested. Grams.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %
Without iodide.	.....	.....	9.30	.....	0.0465	0.465
	10	.....	9.25	1	0.0462	0.462
	20	.....	9.30	2	0.0465	0.465
With iodide.	.....	1	9.30	.....	0.0465	0.465
	20	1	9.25	2	0.0462	0.462

The above results show that no appreciable error was introduced, even without using the iodide indicator, by the presence of 2 grams of sodium carbonate. The finishing point in absence of KI was, however, rather indistinct, and in all cases (with or without KI) a slight whitish turbidity occurred just before the finish.

Tests in which sodium hydrate or ammonia were added, as well as sodium carbonate, gave the correct finishing point when titrated with $AgNO_3$ in presence of KI.

No. 4.—Sodium Carbonate.

Solutions used.

(*a*) Potassium cyanide, 0.715% KCy.
(*b*) Sodium carbonate, 3.78% Na_2CO_3.

(*c*) Potassium iodide (neutral), 1% KI.

(*d*) Silver nitrate, 0.652% $AgNO_3$ (1 c.c. = 0.005 gram KCy).

Details of Test.

Volume of cyanide solution (*a*) in each titration = 10 c.c.
Weight of cyanide in portion tested = 0.0715 gram.

	Volume of Na_2Co_3 sol. (*b*) taken. c.c.	Volume of water added. c.c.	Volume of neutral 1% KI added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of Na_2CO_3 in portion tested. Grams.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %
Without iodide.	.....	.....	.....	14.45	.....	0.0722	0.722
	.....	50	.....	14.4	.....	0.0720	0.720
	25	.....	.....	14.4	0.044	0.0720	0.720
	50	.....	.....	14.5	1.888	0.0725	0.725
With iodide.	.....	.....	5	14.4	.....	0.0720	0.720
	.....	50	5	14.3	.....	0.0715	0.715
	50	.....	5	14.3	1.888	0.0715	0.715
	solid	50	5	14.35	1.000	0.0717	0.717

The solution gave a slight turbidity before the proper finishing point, but otherwise there was no evidence of any interference owing to presence of sodium carbonate.

The apparent strength of cyanide was slightly diminished by dilution.

No. 5.—Ammonium Carbonate.

Solutions used.

(*a*) Pure cyanide, 0.47% KCy.

(*b*) Ammonium carbonate, showing by titration with N/10 acid and methyl orange, 6.288% $(NH_4)_2CO_3$.

(*c*) Potassium iodide (neutral), 1% KI.

(*d*) Silver nitrate, 0.652% $AgNO_3$; 1 c.c. = 0.005 gr. KCy.

Details of Test.

Volume of cyanide solution (*a*) in each titration = 10 c.c.
Weight of cyanide in portion tested = 0.047 gram.

	Volume of $(NH_4)_2CO_3$ sol. (*b*) added. c.c.	Volume of KI sol. (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of $(NH_4)_2CO_3$ in portion tested. Grams.	Weight of K Cy indicated. Grams.	Cyanide indicated in original solution. %
Without iodide.	.....	.....	9.40	.....	0.0470	0.470
	1	.....	9.45	0.063	0.0472	0.472
	5	.....	10.20	0.314	0.0510	0.510
	10	.....	11.10	0.629	0.0555	0.555
	15	.....	11.65	0.948	0.0582	0.582
With iodide.	.....	3	9.35	.....	0.0467	0.467
	10	1	9.20	0.629	0.0460	0.460
	15	3	9.30	0.943	0.0465	0.465

Here the results in presence of iodide show a tendency to appear slightly lower than the truth.

No. 6.—Sodium Bicarbonate.

Solutions used.

(*a*) Potassium cyanide, 0.47% KCy (containing a trace of alkali).

(*b*) Sodium bicarbonate, prepared from commercial salt.

Combined titrations of this solution with decinormal acid, using phenol phthaleïn and afterwards methyl orange, indicated

1.42% Na_2CO_3

1.78% $NaHCO_3$.

(*c*) Potassium iodide (neutral), 1%.

(*d*) Silver nitrate, 0.652% $AgNO_3$; 1 c.c. = 0.005 gram KCy.

(*e*) Nitric acid, N/10, standardized with pure sodium carbonate and methyl orange.

In some of the following tests the carbonate shown to be present in solution (*b*) was neutralized or nearly neutralized with N/10 nitric acid, in accordance with the equation:

$$Na_2CO_3 + HNO_3 = NaHCO_3 + NaNO_3.$$

Details of Test.

Volume of cyanide solution (*a*) in each titration = 10 c.c.

Weight of cyanide in portion tested = 0.047 gram.

	Volume of bicarbonate sol. (*b*) added. c.c.	Volume of N/10 HNO_3 sol. (*e*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of actual $NaHCO_3$ in port'n tested. Grams.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %
Without iodide.	.....	.....	9.40	.....	0.0470	0.470
	5	.....	9.40	0.089	0.0470	0.470
	10	.....	9.35	0.178	0.0467	0.467
	10	12.0	9.25	0.259	0.0462	0.462
	15	.....	9.45	0.267	0.0472	0.472
	15	20.0	9.35	0.435	0.0467	0.467
	20	26.8	9.25	0.581	0.0462	0.462

	Volume of bicarb. sol. (*b*) added. c.c.	Volume of N/10 HNO_3 sol. (*e*) added. c.c.	Volume of KI sol. (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of actual $NaHCO_3$ in port'n tested. c.c.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %
With iodide.	.....	.....	1	9.40	.....	0.0470	0.470
	20	26.8	1	9.30	0.581	0.0465	0.465

In cases where the monocarbonate was exactly neutralized the silver precipitate dissolved rather slowly towards the finish, and sometimes showed a tendency to assume a granular form.

The results in presence of much bicarbonate seem to be slightly lower than the truth.

Tests Illustrating the Influence of Chlorides on the Titration of Cyanides with Silver Nitrate.

No. 1.—Sodium Chloride.

Solutions used.

(*a*) Potassium cyanide, 0.4025% KCy.
(*b*) Sodium chloride (pure crystallized NaCl).
(*c*) Potassium iodide, 10% KI (neutral).
(*d*) Silver nitrate, 0.652% $AgNO_3$; 1 c.c. = 0.005 gram KCy.

Details of Test.

Cyanide solution (*a*) used in each titration = 10 c.c.
Weight of KCy in portion tested = 0.04025 gram.

	Weight of NaCl crystals added. Grams.	Volume of KI sol. (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %	Percentage of error above true value. %
Without iodide.	.....	.....	8.10	0.0405	0.405	0.6
	0.5	.....	8.30	0.0415	0.415	3.1
	1.0	.....	8.50	0.0425	0.425	5.6
With iodide.	.....	1	8.05	0.04025	0.4025	.....
	0.5	1	8.05	0.04025	0.4025	.....
	1.0	1	8.05	0.04025	0.4025	.....

One gram of the sodium chloride (*b*) dissolved in a little water gave an immediate precipitate with a single drop of $AgNO_3$, which did not redissolve on agitation; hence it appears that the error is not due to solubility of silver chloride in sodium chloride.

No. 2.—Ammonium Chloride.

Solutions used.

(*a*) Potassium cyanide, 0.47% KCy.

(*b*) Ammonium chloride, 5.34% NH_4Cl, neutral to phenol phthaleïn and methyl orange.

(*c*) Potassium iodide (neutral), 1% KI.

(*d*) Silver nitrate, 0.652% $AgNO_3$; 1 c.c. = 0.005 gram KCy.

Details of Test.

Cyanide solution (*a*) used in each titration = 10 c.c.

Weight of KCy in portion tested = 0.047 gram.

	Volume of NH_4Cl sol. (*a*) added. c.c.	Volume of KI sol. (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of NH_4Cl in portion tested. Grams.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %
Without iodide.	.....	.....	9.40	.....	0.0470	0.470
	5	.....	9.45	0.267	0.0472	0.472
	10	.....	9.70	0.534	0.0485	0.485
	15	.....	9.70	0.801	0.0485	0.485
	20	.....	9.85	1.068	0.0492	0.492
With iodide.	.....	1	9.40	.....	0.0470	0.470
	5	1	8.85	0.267	0.0442	0.442
	10	1	8.65	0.534	0.0432	0.432
	15	1	8.60	0.801	0.0430	0.430
	20	1	8.50	1.068	0.0425	0.425
	15	3	8.45	0.801	0.0422	0.422
	20	3	8.30	1.068	0.0415	0.415
	20	5	8.00	1.068	0.0400	0.400

From these tests it appears that the presence of ammonium chloride causes the apparent strength of cyanide to be higher than the truth when the solution is titrated without indicator. When neutral KI is added, however, the result is lower than the truth, owing probably to volatilization of ammonium cyanide, and the finish. With ammonium carbonate the results in presence of KI were also somewhat lower than the truth, but the error was less than in the case of the chloride. Addition of sufficient caustic alkali or ammonia, together with the iodide, corrects this error, as seen in the following tests:

Cyanide solution (*a*) used in each case = 10 c.c.
Weight of KCy in portion tested = 0.047 gram.
Volume of NH_4Cl solution (*b*) in each case = 20 c.c.
Weight of NH_4Cl in portion tested = 1.068 grams.

Alkali Added.	Volume of KI sol. (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %
4 c.c. 3.85% NaOH	1	9.2	0.0460	0.460
5 c.c. NH_4OH (10% of strong)	3	9.15	0.0457	0.457
Excess of ammonia	1	9.4	0.0470	0.470

No. 3.—Ammonium Chloride.

Solutions used.

(*a*) Potassium cyanide, 0.725% KCy.
(*b*) Ammonium chloride, 1% NH_4Cl.
(*c*) Potassium iodide (neutral), 1% KI.
(*d*) Potassium iodide (alkaline), 1% KI, 4% NaOH.
(*e*) Silver nitrate, 0.652% $AgNO_3$ (1 c.c. = 0.005 gram KCy).

Details of Test.

Cyanide solution (*a*) taken for each titration = 10 c.c.
Weight of KCy in portion tested = 0.0725 gram.

	Volume of NH_4Cl sol. (*b*) added.	Volume of Iodide indicator added.		Volume of $AgNO_3$ sol. (*e*) required.	Weight of NH_4Cl in portion tested.	Weight of KCy indicated.	Cyanide indicated in original solution.
		Neutral. (*c*)	Alkaline. (*d*)				
	c.c.	c.c.	c.c.	c.c.	Grams.	Grams.	%
Without iodide.	.....	.....	.....	14.5	.....	0.0725	0.725
	15	.....	.....	14.5	0.15	0.0725	0.725
	30	.....	.....	14.5	0.30	0.0725	0.725
	45	.....	.....	14.55	0.45	0.0727	0.727
	65	.....	.....	14.6	0.65	0.0730	0.730
With neutral iodide.	.....	5	.....	14.5	.....	0.0725	0.725
	15	5	.....	14.1	0.15	0.0705	0.705
	30	5	.....	13.9	0.30	0.0695	0.695
	45	5	.....	13.7	0.45	0.0685	0.685
	65	5	.....	13.5	0.65	0.0675	0.675
With alkaline iodide.	65	.....	5	14.3	0.65	0.0715	0.715
	65	.....	10	14.5	0.65	0.0725	0.725

Tests Illustrating the Influence of Ferrocyanides and Sulphocyanides on the Titration of Cyanides by Silver Nitrate, and Correction of the Error by Means of Potassium Iodide.

I.—Ferrocyanides.

Test No. 1.

Solutions used.

(*a*) Cyanide, 0.565% KCy.
(*b*) Potassium ferrocyanide (N/10), $K_4FeCy_6.3H_2O$ = 4.22%.
(*c*) Potassium iodide (neutral), 1% KI.
(*d*) Silver nitrate, $AgNO_3$ 1.304% (1 c.c. = 0.01 gram KCy).

Details of Test.

Cyanide solution (*a*) taken for each titration = 10 c.c.
Weight of cyanide in each portion tested = 0.0565 gram.

	Volume of N/10 ferrocyanide added. c.c.	Volume of 1% KI sol. (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of ferrocyanide present. Grams.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %
Without iodide.	.....	.....	5.60	.....	0.0560	0.560
	5	.....	6.50	0.211	0.0650	0.650
	10	.....	7.05	0.422	0.0705	0·705
With iodide.	.....	5	5.65	.....	0.0565	0.565
	5	5	5.65	0.211	0.0565	0.565
	10	5	5.65	0.422	0.0565	0.565

Test No. 2.

Solutions used.

(*a*) Potassium cyanide, 0.342% KCy.
(*b*) Potassium ferrocyanide, 1% $K_4FeCy_6.3H_2O$.
(*c*) Potassium iodide (alkaline), 1% KI, 4% NaOH.
(*d*) Silver nitrate, 0.652% $AgNO_3$ (1 c.c. = 0.005 gram KCy).

Details of Test.

Cyanide solution (*a*) taken for each titration = 10 c.c.
Weight of cyanide in each portion tested = 0.0342 gram.

	Volume of 1% ferrocyanide (*b*) added. c.c.	Volume of 1% KI sol. (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of ferrocyanide present. Grams.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %
Without iodide.	.....	.....	6.85	.....	0.0342	0.342
	5	.....	7.45	0.05	0.0372	0.372
	10	.....	8.20	0.10	0.0410	0.410
	15	.....	8.50	0.15	0.0425	0.425
	20	.....	8.90	0.20	0.0445	0.445
	25	.....	9.10	0.25	0.0455	0.455
	50	.....	9.25	0.50	0.0462	0.462
With iodide.	20	1	7.20	0.20	0.0360	0.360
	20	3	6.80	0.20	0.0340	0.340
	50	3	7.05	0.50	0.0352	0.352
	50	5	6.80	0.50	0.0340	0.340

II.—Sulphocyanides (Thiocyanates).

Test No. 1.

Solutions used.

(*a*) Potassium cyanide, 0.4% KCy.
(*b*) Ammonium sulphocyanide, 0.5% NH_4CyS.
(*c*) Potassium iodide (alkaline), 1% KI, 4% NaOH.
(*d*) Silver nitrate, $AgNO_3$ 0.652% (1 c.c. = 0.005 gram KCy).

Details of Test.

Cyanide solution (*a*) taken for each titration = 10 c.c.
Weight of cyanide in portion tested = 0.04 gram.

	Volume of .5% sulphocyanide (*b*) added. c.c.	Volume of alk. KI (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of sulphocyanide present. Grams.	Weight of KCy indicated. Grams.	Cyanide indicated in original solution. %
Without iodide.	.....	.....	8.0	.....	0.0400	0.400
	5	.....	8.0	0.025	0.0400	0.400
	10	.....	8.1	0.05	0.0405	0.405
	15	.....	8.05	0.075	0.0402	0.402
	25	.....	8.05	0.125	0.0402	0.402
With iodide.	25	5	8.0	0.125	0.0400	0.400

From this test it appears that small amounts (up to 0.1 gram) of ammonium sulphocyanide do not appreciably affect the result of the titration.

Test No. 2.

Solutions used.

(*a*) Potassium cyanide, 0.465% KCy.
(*b*) Ammonium sulphocyanide (crystals), NH_4CyS.
(*c*) Potassium iodide, (Alkaline indicator), KI 1%; NaOH 4%.
(*d*) Silver nitrate, 0.652% $AgNO_3$ (1 c.c. = 0.005 gram KCy).

Details of Test.

Cyanide solution (*a*) taken for each titration = 10 c.c.
Weight of cyanide in portion tested = 0.0465 gram.

	Weight of NH_4CyS crystals added. Grams.	Volume of alk. KI sol. (*c*) added. c.c.	Volume of $AgNO_3$ sol. (*d*) required. c.c.	Weight of KCy indicated. Grams.	*Corrected weight of KCy. Grams.	Cyanide indicated in original solution. %
Without iodide.	.....	.....	9.30	0.0465	0.0465	0.465
	1	.....	15.05	0.0752	0.0740	0.740
With iodide.	1	5	9.40	0.0470	0.0458	0.458

* This correction was made because it was found that 1 gram of the NH_4CyS dissolved in a little water, to which 5 c.c. of the alkaline iodide indicator were added, required 0.25 c.c. of $AgNO_3$ to give a distinct turbidity, this result being possibly due to the presence of a trace of free cyanide in the salt used.

The test shows that large quantities of sulphocyanide may cause a serious error, which, however, is corrected by the alkaline iodide indicator.

Test No. 3.

Solutions used.

(*a*) Potassium cyanide, 0.765% KCy.
(*b*) Potassium sulphocyanide, 0.5% KCyS.
(*c*) Potassium iodide (neutral), 1% KI.
(*d*) Silver nitrate, 0.652% $AgNO_3$ (1 c.c. = 0.005 gram KCy).

Details of Test.

Cyanide solution (*a*) taken for each titration = 10 c.c.
Weight of cyanide in portion tested = 0.0765 gram.

	Volume of KCyS sol. (*b*) added. c.c.	Volume of neutral KI added. c.c.	Volume of $AgNO_3$ (*d*) required. c.c.	Weight of KCyS in portion tested. Grams.	Weight of cyanide indicated. Grams.	Cyanide indicated in original solution. %	
Without iodide.	.....	.....	15.4	.....	0.0770	0.770	
	10	.....	15.35	0.05	0.0767	0.767	
	20	.....	15.45	0.10	0.0772	0.772	
	30	.....	15.4	0.15	0.0770	0.770	
	40	.....	15.4	0.20	0.0770	0.770	
	50	.....	15.35	0.25	0.0767	0.767	
	solid	.....	18.5	1.00	0.0925	0.925	
	solid	.....	15.7	1.00	0.0785	0.785	50 c.c. water added.
With iodide.	.....	5	15.3	.....	0.0765	0.765	
	50	5	15.2	0.25	0.0760	0.760	
	solid	5	15.3	1.00	0.0765	0.765	

Tests Illustrating the Influence of Thiosulphates (Hyposulphites) on the Titration of Cyanides with Silver Nitrate.

Solutions used.

(*a*) Cyanide, 0.286%.
(*b*) Sodium thiosulphate (N/10), $Na_2S_2O_3.5H_2O = 2.48\%$.
(*c*) Potassium iodide (neutral), 1% KI.
(*d*) Potassium iodide (alkaline), 4% NaOH, 1% KI.
(*e*) Potassium iodide (ammoniacal), 1% KI.
(*f*) Silver nitrate, 1 c.c. = 0.005 gram KCy; $AgNO_3$, 0.652%.

Details of Test.

Cyanide solution (*a*) taken for each titration = 10 c.c.
Weight of cyanide in each portion tested = 0.0572 gram.

	Vol. of N/10 thiosulphate added.	Volume of Iodide Indicator added.			Volume of $AgNO_3$ sol. required.	Weight of thiosulphate present.	Weight of KCy indicated.	Cyanide indicated in original solution.
		(*c*) Neutral.	(*d*) Alkaline.	(*e*) Ammoniacal.				
	c.c.	c.c.	c.c.	c.c.	c.c.	Grams.	Grams.	Grams.
Without iodide.	.....	.....	.....	.....	11.5	.....	0.0575	0.287
	1	.....	.....	.....	12.8	0.0248	0.0640	0.320
	5	.....	.....	.....	19.4	0.124	0.0970	0.485
	10	.....	.....	.....	29.75	0.248	0.1487	0.744
With iodide.	.....	1	.....	.....	11.45	.....	0.0572	0.286
	10	5	.....	.....	12.9	0.248	0.0645	0.322
	10	10	.....	.....	12.5	0.248	0.0625	0.312
	10	.....	5	.....	12.5	0.248	0.0625	0.312
	10	.....	10	.....	12.0	0.248	0.0600	6.300
	10	.....	15	.....	12.0	0.248	0.0600	0.300
	20	.....	10	.....	12.8	0.496	0.0640	0.320
	10	.....	.....	10	12.6	0.248	0.0630	0.315

(*C*) *Liebig's Method with Potassium Ferrocyanide as Indicator.*

W. Bettel proposes the following method (*Proceedings* Chem. and Met. Soc. of South Africa, Vol. I., p. 165, August 17, 1895):

"Fifty c.c. of solution is taken and titrated with silver nitrate to faint opalescence (or first appearance of a flocculent precipitate). This will indicate (if sufficient ferrocyanide be present to form a

flocculent precipitate of zinc ferrocyanide) the free cyanide, and cyanide equal to 7.9 per cent. of the potassic zinc cyanide.

W. J. Sharwood (*Engineering and Mining Journal,* 1898, p. 216), also, adopts the same process and uses a few drops of a 5 per cent ferrocyanide solution as indicator.

The value of this method, however, is more than doubtful, as may be judged from the following remarks by Mr. Bettel (*loc. cit,* p. 163), on the reactions taking place in presence of the zinc-double cyanide:

"On titration with nitrate of silver the end-reaction is painfully indefinite. . . . . If to a solution of potassic zinc cyanide be added a small quantity of ferrocyanide of potassium and the silver solution run in, the flocculent precipitate of what I suppose to be normal zinc ferrocyanide (Zn_2FeCy_6) appears; the end-reaction is fairly sharp, and indicates 19.5 parts of cyanide of potassium out of the actual molecular contents of 130.2 KCy. If, however, an excess of ferrocyanide be present, the flocculent precipitate does not appear, but in its place one gets an opalescence which speedily turns to a finely granular (sometimes slimy) precipitate of potassic zinc ferrocyanide, $K_2Zn_3Fe_2Cy_{12}$. This introduces a personal equation into the analysis of such a solution, for, if the silver solution be added rapidly, the results are higher than if added drop by drop, as this ferrocyanide of zinc and potassium separates out slowly in dilute solutions alkaline or neutral to litmus paper."

The finishing point, in presence of zinc, is also very seriously affected by dilution, as shown by G. A. Goyder (*Chemical News,* Vol. LXXII., p. 80). (See also below.)

Bettel's quantity ("cyanide equal to 7.9 per cent. of the potassic zinc cyanide present") arises as follows: Assuming 247 as the molecular weight of K_2ZnCy_4, and that, of this weight, 19.5 parts are indicated by the test as free KCy, we have the proportion:

$$19.5 : 247 :: 7.9 : 100.$$

Dr. T. Kirke Rose (*Metallurgy of Gold,* 4th ed., p. 398), commenting on Goyder's observations as to the effect of dilution, quoted below, remarks as follows: "Bettel's amount, 7.9 per cent of the double cyanide, probably, therefore, corresponds only to one definite concentration. The double cyanide is doubtless dissociated more or less into $2KCy + ZnCy_2$ in dilute solutions, and the potassium cyanide set free is perhaps available, both to dissolve gold and to keep silver cyanide remaining dissolved in the water in which it is not

quite insoluble. . . . . In any case it seems quite likely that the free cyanide shown by simple titration represents the cyanide available for the dissolution of gold, so that, from the practical point of view, no new methods are necessary."

Considering the extreme indefiniteness of the indications generally obtained in all attempts to estimate free cyanide in presence of zinc, this last conclusion can hardly be accepted.

(*D*) *Estimation of Free Cyanide by Titration, as in Liebig's Method, after Neutralizing Alkali and Adding Potassium Iodide.*

In mixtures containing both zinc double cyanide and free cyanide, two points may in general be observed on titrating with silver nitrate in presence of potassium iodide: (*a*) The first appearance of a permanent (flocculent) whitish turbidity; (*b*) The appearance of a distinct yellowish coloration or precipitate.

In strongly alkaline solutions the second point corresponds, as will be shown later, with total cyanide.

In solutions containing no free alkali, or only moderate amounts, it is decidedly lower than the amount required for total cyanide.

In solutions containing no free alkali, the first appearance of a flocculent precipitate, in presence of potassium iodide, gives a reading which is, in general, slightly higher than the theoretical contents of the solution in free cyanide. The point is fairly definite, and although not absolutely satisfactory, appears to be the most reliable method so far described for determining this quantity in presence of zinc. It is possible that an actual dissociation of the K_2ZnCy_4 into KCy and $ZnCy_2$ may take place to some extent, and that the test correctly indicates the free cyanide. In some solutions the numbers obtained correspond closely with the theoretical values.

Neutralization of the Solution.—If the solution should contain free alkali, it may be prepared for this test by the following preliminary operations:

(*i*) A test is made for total cyanide by taking a measured portion of the liquid, making strongly alkaline, adding KI, and titrating with $AgNO_3$ till a distinct yellow turbidity is produced.

(*ii*) Another portion of the original liquid is taken, and slightly more than the amount of silver nitrate shown to be necessary by the previous test is added, together with a slight excess of potassium ferrocyanide. A few drops of phenol phthaleïn are added

to the turbid liquid, and the mixture titrated (without filtering) with N/10 acid, until the pink tint just disappears.

(*iii*) A third portion of the original liquid (say 50 c.c.) is taken, and the amount of N/10 acid shown to be necessary by test (*ii*) is gradually added, with agitation, from a burette. Five c.c. of neutral 1 per cent potassium iodide are then added, and the mixture titrated with $AgNO_3$ until a distinct flocculent precipitate (white) remains permanent after agitation and standing for about half a minute. No notice need be taken of an obscure cloudiness which may appear in the liquid at an earlier stage.

The following are some results obtained with solutions prepared by mixing known volumes of simple cyanides, zinc double cyanides, and other substances occurring in working solutions (ferrocyanides, thiocyanates, chlorides, etc.).

Theoretical Contents.			Value of free cyanide obtained by white turbidity in presence of KI in neutralized solution.	
Zinc. %	Total cyanide. %	Free cyanide. %	KCy. %	
.039	.626	.470	.46	(10 c.c. taken)
.....	.....	.....	.465	(15 c.c. taken)
.....	.....	.....	.461	(25 c.c. taken)
.04	1.235	1.075	1.13	(mean of 4 tests)
.045	.611	.431	.472	
.....	.....	.....	.457	
.07	.612	.332	.365	(mean of 5 tests)
.095	.614	.234	.278	(mean of 5 tests)
.05	.4	.2	.199	

(*E*) *Estimation of Free Cyanide by Liebig's Method in Presence of Soluble Sulphides.*

As above noted, the presence of sulphides in the liquid to be tested entirely vitiates the result, owing to the immediate formation of silver sulphide.

(*i*) *Correction by Means of Lead Salts.*—In March, 1893, Messrs. J. S. McArthur and C. J. Ellis patented a process for removing alkaline sulphides from cyanide solutions by the use of various metallic salts, recommending especially salts or compounds of lead, such as plumbates, carbonates, acetates and sulphates. They also instanced the sulphate and chloride of manganese, zincates, oxide and chloride of mercury, and ferric hydrate or oxide. They also applied lead salts for this purpose in the testing of solutions.

Carbonate of lead is probably the most convenient substance to use, as it introduces no soluble salts which might interfere with the subsequent titration. The solution to be tested is agitated with small quantities of carbonate of lead (best freshly precipitated) until further addition gives no black or brown coloration to the liquid. After settling, the clear solution (or an aliquot portion of it) is filtered off and tested in the ordinary way. The reaction is as follows:

$$PbCO_3 + K_2S = PbS + K_2CO_3.$$

Litharge may be employed instead of carbonate of lead with almost equally good results.

If a soluble salt of lead be used, it will be necessary to take a measured volume of the original liquid, add a slight excess of the lead salt, make up to a definite volume, allow to settle, and filter off an aliquot part. If lead acetate be employed it is necessary to remove any excess by the addition of an alkaline carbonate before finally making up to a definite volume, otherwise a portion of cyanide might be precipitated as $PbCy_2$.

In case the finishing point should not be clearly defined, owing to a faint turbidity appearing before the true finish, it is advisable to add a little ammonia and potassium iodide before titrating with silver nitrate.

(*ii*) *Correction by Means of Iodine.*—W. J. Sharwood (*Journal* Amer. Chem. Soc., 1897, p. 400) describes the following process:

"A promising method for the removal of sulphide was based on the fact that a weak solution of iodine precipitates sulphur from alkaline sulphides, this redissolving in a minute or two to form thiocyanate, as the direct decomposition of potassium cyanide by iodine under these conditions approximates to the reaction:

$$2I + KCN = KI + ICN$$

and with K_2S and KCN together:

$$(1) \quad 2I + K_2S = 2KI + S$$

$$(2) \quad S + KCN = KCNS$$

so that two atoms of iodine in either case decompose one molecule of cyanide, and it seemed probable that the interference of small quantities of sulphide could be corrected by adding a constant amount (a slight excess) of a weak iodine solution and introducing a correction for the amount of added iodine, which correction should be independent of the amount of sulphide oxidized. A number of preliminary experiments confirmed this, subsequent titration with

$AgNO_3$ giving, with the correction, quite accurate determinations of the cyanide taken, when the amount of sulphide was small and other reducing agents were absent;* with larger proportions of sulphide an appreciable error was introduced, the extent and variation of which were not determined."

In cases where the amount of sulphide is large or where other reducing agents are also present, Sharwood recommends the following: "Take twice the usual volume of solution, add some soda, then sodium plumbite in very slight excess, shake well, make up to a definite volume, filter, and use half the clear filtrate for titration, rejecting the first few c.c. filtered. In presence of zinc, add a considerable excess of caustic soda or potash."

Method No. 2.

Estimation of Free Cyanide by Means of a Solution of Iodine in Iodide of Potassium.

This process depends upon the fact that when a solution of iodine in potassium iodide is added to a solution of a simple cyanide, the reddish-brown color of the iodine solution disappears so long as the cyanide is in excess, since the reaction results in the formation of an iodide of an alkali metal and cyanogen iodide, both of which are colorless:

$$KCy + I_2 = KI + ICy.$$

The finish of the reaction is sharply marked by the permanence of the yellowish tint in the solution under examination, after agitation.

The end-reaction may be made even more distinct by using a drop of the starch indicator prepared as follows:

One part of pure, fresh starch is rubbed into a thin paste with a little cold water, then gradually poured into 150 to 200 times its weight of boiling water, the boiling continued for a few minutes, and the liquid then allowed to stand and settle. Only the clear solution is used for the indicator. The finishing point is now marked by the permanence of an intense blue or bluish-violet tint. The starch solution does not retain its sensitiveness for long, and must generally be freshly prepared. The substances sometimes

* It would apparently be simpler, in such cases, to determine the cyanide by the 'iodine method' of Fordos and Gélis, rather than to complete the titration by Liebig's method.

added to preserve it, *e.g.*, caustic alkalis, zinc chloride and mercuric iodide, would be inadmissible for testing cyanide solutions.

An iodine solution, suitable for cyanide titrations, may be prepared by dissolving 3.899 grams of chemically pure iodine and about 6 grams of potassium iodide in a small volume of water, and diluting with distilled water to 1,000 c.c. With this solution, 1 c.c. iodine = 0.001 gram KCy.

It is not necessary, in practice, to prepare chemically pure iodine, as the solution may be very conveniently standardized by means of a solution of pure potassium cyanide, the strength of which has been accurately ascertained by Liebig's (silver nitrate) method. The value of the iodine solution is thus made to depend on the accuracy of the standard silver solution. For cyanide testing, this method of standardizing is more convenient than the usual method with standard thiosulphate, and probably quite as accurate, if not more so, since nitrate of silver is easily obtained in a condition of great purity.

The method of titration with iodine is described by Fordos and Gélis (*Journal de Chim. et de Pharm.*, 23, 48), and generally ascribed to them, but the reaction on which it depends appears to have been originally mentioned by Serullas and Wöhler (Fresenius, *Quant. Anal.*, 7th ed., 1876, Vol. I., p. 375).

Limitations of the Method.—This process is, of course, not applicable where other substances are present which are also capable of reacting on iodine, but in some cases such interfering substances may be removed, as described below.

The iodine method is useful in certain cases where the solution is free from zinc, but turbid with suspended matter which cannot conveniently be removed by filtration. With such a solution, titration with silver nitrate would be difficult, if not impossible, as the end-point could not be accurately observed. When the starch indicator is used, the end-point with iodine is quite distinct, even in turbid solutions.

In presence of the zinc double cyanide the finishing point is uncertain and indefinite. A white precipitate occurs gradually at a certain stage of the titration, probably consisting of zinc cyanide, as follows:

$$K_2ZnCy_4 + 2I_2 = ZnCy_2 + 2KI + 2ICy.$$

The substances commonly occurring in cyanide solutions which interfere with the iodine process are caustic alkalis, monocarbonates,

ammonia, sulphides, thiosulphates, and probably most organic reducing agents. Ferrocyanides, ferricyanides and thiocyanates (sulphocyanides) do not interfere. According to W. J. Sharwood, small quantities of sulphides do not interfere, since the sulphur liberated combines with an equivalent of cyanide. (See above.)

The procedure in presence of alkalis is described below.

Estimation of Free Cyanide by Iodine in Presence of Alkalis.

In the presence of alkalis the finishing point with iodine becomes very indefinite, and, moreover, represents more than the amount of free cyanide present.

It was originally recommended to add carbonic acid water (ordinary soda water), in order to convert both hydrates and monocarbonates into bicarbonates, for example:

$$KOH + CO_2 = KHCO_3.$$
$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3.$$

Since bicarbonates have no action on iodine, the solution may now be titrated by standard iodine, and the amount of cyanide correctly determined.

Bettel (*Proceedings* Chem. and Met. Soc. South Africa, Vol. I., p. 219) recommends adding 50 c.c. of ordinary soda water to the solution to be tested, and titrating at once with decinormal or centinormal iodine.

It is evident, however, that any excess of carbonic acid will decompose cyanide with liberation of hydrocyanic acid, thus:

$$KCy + CO_2 + H_2O = KHCO_3 + HCy,$$

though probably with dilute solutions, if titrated at once, the effect of a small excess of CO_2 would not be very noticeable.

However, the following method (*Proceedings* Chem. and Met. Soc. South Africa, Vol. I., p. 205) gives accurate results, and avoids the danger of loss from the use of excess of acid:

To a measured volume of the solution silver nitrate is first added until a permanent turbidity is produced, the exact amount added being of no consequence. A drop of phenol phthaleïn is now added to this somewhat turbid solution, and standard acid (for example, N/10 H_2SO_4, HCl or HNO_3) is added until the pink color just disappears. The amount required represents, as will be shown later, the quantity of acid necessary to convert hydrates into neutral salts, and monocarbonates into bicarbonates, without any decomposition

of cyanide taking place. If, now, we take a fresh measured volume of the original solution and add to it, with agitation, the quantity of dilute acid shown to be necessary by the previous experiment, we obtain a solution which may at once be titrated with iodine.

Method No. 3.

Estimation of Free Cyanide by Means of a Solution of Mercuric Chloride.

J. B. Hannay (*Journal* Chem. Soc., 1878, Vol. I., p. 245) describes this method for examination of commercial cyanides. It depends upon the fact that when mercuric chloride is added to a solution of free cyanide containing ammonia, the precipitate first formed is redissolved as long as the cyanide is in excess, the reactions being probably as follows:

(*a*) Precipitation of white mercur-ammonium chloride:

$$HgCl_2 + 2NH_3 = NH_4Cl + NH_2HgCl.$$

(*b*) This precipitate dissolves, on agitation, as long as cyanide is in excess.

$$NH_2HgCl + NH_4Cl + 2KCy = HgCy_2 + 2KCl + 2NH_3.$$

(*c*) When no more free cyanide remains, further addition of $HgCl_2$ gives a permanent precipitate according to reaction (*a*).

Since, from these reactions, one molecule of $HgCl_2$ is equivalent to two of KCy, 27.092 parts of mercuric chloride are required for 13.022 parts of potassium cyanide. Hence if a solution be prepared containing 20.806 grams mercuric chloride per liter, then 1 c.c. mercuric solution = 0.01 gram of KCy. The ordinary N/10 solution of mercuric chloride contains 13.546 grams per liter. Hence 1 c.c. of this = 0.006511 gram KCy.

The method of titrating is as follows (Sutton, *Volumetric Analysis,* 8th ed., p. 217):

"The vessel containing the solution to be tested is placed upon black paper or velvet; ammonia is then added in moderate quantity and the mercuric solution cautiously added, with constant stirring, until a bluish-white opalescence is permanently produced."

Hannay states that alkaline sulphates, nitrates and carbonates, caustic alkalis, cyanates and thiocyanates have no effect on the estimation of cyanide by this method. He further states that if silver nitrate be added, and then ammonia to dissolve the precipitate, if any, the cyanogen may still be completely estimated by titration with

mercuric chloride. Hence any cyanogen present in the solution as $KAgCy_2$ would be determined as free cyanide, a result which would render the method useless for many practical purposes.

The finishing point is much less definite than in the silver nitrate or iodine methods. I find that a solution of 1 per cent potassium iodide and 4 per cent caustic soda makes a much better indicator than ammonia, 1 c.c. of this indicator being added for every 10 c.c. of cyanide solution taken for the test, the end-point being marked by the permanence of a slight yellowish tinge.

Method No. 4.

Estimation of Free Cyanide by Means of an Ammoniacal Solution of a Copper Salt.

This is merely a reversal of the well-known method for the estimation of copper by means of standard potassium cyanide. A solution is prepared by adding ammonia to a pure solution of sulphate or nitrate of copper until a clear, deep blue liquid is obtained. This is standardized by running into a measured volume of pure cyanide solution of known strength until a faint purplish tint remains permanent. An equal volume of the solution to be tested is then immediately titrated in the same way. The strength of the standard solution must be checked frequently against pure cyanide. I have found it generally preferable to add the copper solution in slight excess and determine the excess by means of the standard cyanide solution.

This method is, of course, subject to the indefiniteness as to the exact finishing point which characterizes the determination of copper by this means. In presence of zinc the reading obtained indicates much more than the free cyanide, but does not give the whole of the cyanogen present as K_2ZnCy_4.

Method No. 5.

Estimation of Free Cyanide by Titration with Standard Acid.

Potassium cyanide is alkaline to most indicators, such as litmus, phenol phthaleïn and methyl orange. Hence the amount of cyanide in a pure solution may be estimated by simple titration with an acid until the completion of the reaction, *e.g.*,

$$2KCy + H_2SO_4 = K_2SO_4 + 2HCy.$$

In the case of litmus and phenol phthaleïn, the finishing point is not quite sharp, as the indicators are affected to some extent by the hydrocyanic acid liberated during the titration. With methyl orange tolerably accurate determinations may be made. When alkaline hydrates and carbonates are present these must be separately determined and a correction made. This matter will be fully discussed in treating of the estimation of alkalis in cyanide solutions. Bicarbonates are alkaline to methyl orange, but neutral to the other indicators. It may here also be remarked that the double cyanide of zinc and potassium is completely alkaline to methyl orange, and partially to phenol phthaleïn.

The method cannot be recommended for practical use owing to the numerous corrections necessary, but Goyder (*Chemical News*, Vol. LXXII., p. 81) has attempted to apply it as follows:

"The titration is made by measuring 100 c.c. of sump solution, or solution after passing through the tailings into a stoppered bottle, adding 1 c.c of 1/20 per cent phenol phthaleïn, and running in N/10 hydrochloric acid till the pink color is destroyed."

1 c.c. N/10 acid = 0.0065 gram KCy.

John Longmaid (*Engineering and Mining Journal*, May 11, 1895, p. 435) describes an experiment which shows that under certain conditions a solution which has passed through a charge of ore may become perfectly neutral to phenol phthaleïn while still appearing to contain large amounts of free cyanide. The experiment, however, is inconclusive, as nothing is said as to the nature of the foreign salts present in the solution after use, and this solution may easily have contained considerable quantities of hydrocyanic acid. The writer's contention that the alkalinity of cyanide solutions towards phenol phthaleïn is due to a trace of caustic potash is untenable, since the percentage of cyanogen may be quantitatively determined in pure solutions by means of N/10 acid and phenol phthaleïn. (See Appendix, page 161.)

SECTION 2.

Estimation of Total Cyanide.

For the purpose of this investigation, the term 'total cyanide' will be used to indicate the equivalent in potassium cyanide of all the cyanogen existing in the form of simple cyanides, hydrocyanic

acid and the double cyanides of zinc. In one of the methods to be described, the cyanogen present in certain other easily-decomposed double cyanides would likewise be included, *e.g.*, those of silver and mercury. Methods in which the cyanogen present as ferrocyanides, ferricyanides and sulphocyanides (thiocyanates) is also included will be discussed later under 'Estimation of Total Cyanogen.'

The chief methods proposed are:

1. Titration with silver nitrate after addition of an excess of caustic alkali.
2. Titration with iodine in presence of an excess of ferrocyanide.
3. Titration with silver nitrate after decomposition of double cyanides by means of alkaline sulphide.

Method No. 1.

Estimation of Total Cyanide by Titration with Silver after Addition of Excess of Caustic Alkali.

When a sufficient quantity of caustic alkali has been added to a solution containing zinc double cyanide, simple cyanides of the alkali and alkaline earth metals, or hydrocyanic acid, the whole of the cyanogen existing in all or any of these forms may be determined by titration with silver nitrate. To obtain accurate results it is necessary to use the potassium iodide indicator. The amount of caustic alkali to be added will, of course, depend on the amount of zinc present, but an excess is of no consequence. Usually about 10 c.c. of normal NaOH will be sufficient. For regular use it is convenient to employ an indicator consisting of 4 grams NaOH and 1 gram KI dissolved to 100 c.c. in distilled water. From 5 to 10 c.c. of this solution are added for each test. The finishing point is generally quite sharp and definite, and is shown by a permanent yellowish tint. In some cases, as pointed out by L. M. Green (*Inst. Min. and Met.*, October 17, 1901), a white cloudiness occurs before the true finishing point, probably due to precipitation of zinc ferrocyanides. I find that in most cases this may be entirely prevented by the addition of a little ammonia. So far as I have been able to ascertain, this method, which is undoubtedly the best for determining total cyanide in practice, was suggested by the observation of W. R. Feldt-

mann (*Engineering and Mining Journal,* Vol. LVIII., 1894, pp. 218-219) that "addition of alkali to working solutions which have become somewhat weak in alkali brings up the strength by regenerating (*i.e.,* decomposing) the zinc cyanide, so that, as a matter of fact, when the solutions are pretty strongly alkaline they contain no zinc as cyanide, but only as hydrate dissolved in alkali (zincate of potash, etc.)." This explanation is probably erroneous, as will be shown below, but it is very probable that it suggested the methods described almost simultaneously by G. A. Goyder (*Chemical News,* Vol. LXXII., p. 80) and W. Bettel (*Proceedings* Chem. and Met. Soc. South Africa, Vol. I., p. 165), in both of which the addition of potassium iodide is recommended.

Goyder proceeds as follows: "Ten c.c. of 5 per cent NaOH is mixed with 20 c.c. of the sump solution. If a precipitate is formed, 15 c.c. of the mixture is filtered off and titrated, after addition of potassium iodide, with standard silver solution" (15 c.c. solution). He says, further, that the percentage thus obtained indicates cyanogen present as free cyanide, zinc double cyanide, and some other double cyanides, but does not include ferrocyanides or the double cyanides of mercury or copper.

Bettel adds caustic alkali in excess (a few c.c. of normal caustic soda) to 50 c.c. of the solution to be tested, and a few drops of a 10 per cent solution of potassic iodide, and titrates to opalescence with $AgNO_3$. This gives free cyanide, hydrocyanic acid, and double cyanides such as zinc potassium cyanide, but not ferrocyanides or sulphocyanides.

W. J. Sharwood (*Journal* Amer. Chem. Soc., 1897, pp. 400-434) discusses this method of titration in detail, and says: "If zinc be present, a large excess of alkali should be added; in this case the cyanogen found represents not only the potassium cyanide, but also the double zinc compound. By estimating the zinc, the amount of free potassium cyanide may be readily calculated as 1 part of zinc corresponds with 4 parts of potassium cyanide. A similar allowance must be made if small quantities of copper are present. If calcium, magnesium or manganese are present, ammonium chloride must be added, whilst soda is used in presence of aluminium or lead." He also recommends the addition of ammonia (*Engineering and Mining Journal,* 1898, p. 216): "Total cyanogen was obtained by continuing the titration with silver after addition of caustic soda and a little

ammonia and potassium iodide; this, however, does not include cyanogen in double cyanides of copper, silver, gold and mercury."

Nature of the Reaction in Presence of Zinc.—The precise nature of the reaction taking place when caustic alkalis are added to solutions containing zinc double cyanide has given rise to much discussion. According to Feldtmann's observations, quoted above, it should, apparently, be:

$$K_2ZnCy_4 + 4KOH = Zn(OK)_2 + 4KCy + 2H_2O.$$

As, however, the reverse reaction undoubtedly takes place, it seems uncertain whether free potassium cyanide and potassium zincate can coexist in the same solution.

Goyder (*Chemical News,* Vol. LXXII., p. 80), commenting on Feldtmann's observation, remarks: "But I believe that caustic alkali is never added in large excess to the lixiviating solutions, and when added in small quantities the double decomposition would not be complete, and its amount could only be calculated by applying the laws of chemical mass-action after finding the relative proportion of the double cyanide of zinc and potassium to caustic alkali, and the velocity of combination of the resulting salts. As, in practice, this problem is complicated by the presence of the double salts and caustic potash, as well as other salts, its solution is probably impossible. It may, however, be taken for granted that when caustic alkali is added to a solution of double cyanide of potassium and zinc in molecular proportions, the resulting solution will, after a little time, contain zincate of potash, cyanide of potassium and the double salt."

Bettel (*Proceedings* Chem. and Met. Soc., South Africa, Vol. I., p. 167) also gives the reaction between zinc double cyanide and caustic alkali as above, and also the analogous reaction for alkaline carbonates:

$$K_2ZnCy_4 + 4Na_2CO_3 + 2H_2O = 2KCy + 2NaCy + Zn(NaO)_2 + 4NaHCO_3.$$

J. S. C. Wells, however (*Engineering and Mining Journal,* Vol. LX., p. 584), states definitely that K_2ZnCy_4 is not decomposed by alkali into free KCy and potassium zincate.

Charles J. Ellis (*Journal* Soc. Chem. Ind., January 28, 1897, p. 117) remarks as follows:

"I have proved the following reactions to take place on adding silver nitrate to a solution of double zinc cyanide in absence of free alkali:

$ZnCy_2 \cdot 2KCy + AgNO_3 = AgCyKCy + KNO_3 + ZnCy_2$, and
$ZnCy_2 \cdot 2KCy + 2AgNO_3 = 2AgCy + 2KNO_3 + ZnCy_2$."

[I may here mention that I have on several occasions verified this observation. The precipitate formed by adding to a solution of K_2ZnCy_4 half the amount of silver nitrate required for determination of total cyanide by the process under discussion, when collected and carefully washed, was found to consist exclusively of zinc cyanide $ZnCy_2$.]

"We may suppose the following reactions to take place simultaneously in presence of caustic alkali:

(*a*) $2\{ZnCy_2 \cdot 2KCy\} + 2AgNO_3 = 2AgCyKCy + 2KNO_3 + 2ZnCy_2$.

(*b*) $2ZnCy_2 + 4KOH = ZnCy_2 \cdot 2KCy + ZnOK_2O + 2H_2O$.

The potassic cyanide portion of the double zinc cyanide, re-formed as in (*b*) being acted upon further by the silver salt as in (*a*), this going on until all the zinc is brought into the form of zinc-potassic oxide."

The observations of Wells and Ellis show that it is not at all necessary to assume any such decompositions as those given by Feldtmann, Goyder and Bettel. The formation of zincate may be considered as taking place only on addition of sufficient silver nitrate, the entire reaction being expressible as follows:

$$K_2ZnCy_4 + 4KOH + 2AgNO_3 = 2KAgCy_2 + Zn(OK)_2 + 2KNO_3 + 2H_2O.$$

Or, in the case of carbonates,

$$K_2ZnCy_4 + 4Na_2CO_3 + 2AgNO_3 + 2H_2O = 2KAgCy_2 + Zn(ONa)_2 + 2NaNO_3 + 4NaHCO_3.$$

Bettel gives the following equation, in absence of caustic or carbonated alkalis:

$$20K_2ZnCy_4 + 3AgNO_3 = 3KAgCy_2 + 3KNO_3 + 2[(ZnCy_2)_{10}(KCy)_{17}].$$

Disturbing Factors in the Titration of Solutions Containing Zinc. —G. A. Goyder (*Chemical News,* Vol. LXXII., p. 80) makes the following remarks on titration in presence of zinc cyanide:

"In titrating the sump solutions which contain much of their cyanogen as the double cyanide of zinc and potassium, the end-reaction was not only ill-defined, but the quantity of nitrate of silver required to produce a permanent turbidity increases with dilution, with the temperature, and also with the amount of simple cyanide added to a greater extent than was calculated. . . . A cold sump solution to which nitrate of silver has been added to

permanent turbidity always clears on being heated. As regards the indefiniteness of the reaction, a sample of sump solution was divided into three equal portions. To No. 2 an equal volume and to No. 3 two volumes of distilled water were added, and these were given to an expert well acquainted with the process, but not knowing how the solutions were made up to test. He reported that No. 1 contained 0.04 per cent, No. 2, 0.05 per cent and No. 3, 0.04 per cent of simple cyanide." A solution which, when tested, appeared to contain 0.02 per cent was strengthened by the addition of more cyanide until it should, by calculation, have contained 0.09 per cent. The actual test, however, indicated a strength of 0.15 per cent.

The indication in presence of zinc, when an excess of alkali is not added, thus appears to be a function, not only of the free cyanide, but also of (*a*) the degree of dilution; (*b*) the temperature; (*c*) the rate of titration; (*d*) the amount of zinc present; (*e*) the amount of ferrocyanide present.

In a given solution, provided it can be obtained perfectly clear, it is possible to distinguish the following indications with silver nitrate:

1. The first indication of a flocculent precipitate, on titrating a measured quantity (undiluted) with $AgNO_3$ without indicator. This can be observed, although with some difficulty, with a pure solution of K_2ZnCy_4.

2. The indication in presence of neutral potassium iodide—generally slightly higher than No. 1.

3. The indication in presence of a slight excess of ferrocyanide.

4. The indication with excess of caustic alkali and potassium iodide.

5. The indication with ammonia and potassium iodide.

To these might be added:

6. The indication with neutral potassium chromate as indicator. This will be discussed later.

Titration of Cyanide in Solutions Containing Copper.—According to the observations of Goyder and Sharwood (quoted above) any cyanogen existing as double cyanide of copper and potassium will not be determined at all when the potassium iodide indicator is used. A marked difference is observed in the result, according as potassium iodide is added or not. This matter has been discussed in considerable detail by W. H. Virgoe (*Proceedings* Inst. Min. and Met., Vol., X., p. 102) and myself (*Journal* Soc. Chem. Ind., Vol. XIX.,

p. 14). Hence it appears that, when titrated without addition of potassium iodide, a certain proportion of the cyanogen of the copper salt is determined as though it were free KCy. The amount so determined is increased by dilution or addition of alkalis. In solutions containing no free alkali, about 3/14 of the total cyanide of the copper salt is determined by titration with $AgNO_3$ without indicator (assuming that no portion of it is determined by titration in presence of KI). The end-point in presence of the iodide is slightly affected by dilution, but is not altered by the presence of alkali. The average of a large number of experiments showed that 3.5 parts of KCy are consumed (or at least rendered incapable of reacting with silver nitrate in presence of KI) for every part of copper dissolved, when the copper salt is prepared with precautions to prevent loss of cyanogen.

A tentative explanation of these reactions may be based on the assumption that cuprous cyanide, Cu_2Cy_2, forms molecular compounds with KCy. Thus we may suppose the reaction of cyanide on cupric hydrate to be as follows:

$$2Cu(HO)_2 + 7KCy = 4KCy\cdot Cu_2Cy_2 + KCyO + 2KOH + H_2O$$

When silver nitrate is added to the solution of this double salt, a portion only of the combined potassium cyanide is capable of reacting to form the soluble double cyanide of silver:

$$4KCy\cdot Cu_2Cy_2 + AgNO_3 = KAgCy_2 + 2KCy\cdot Cu_2Cy_2 + KNO_3$$

Silver nitrate thus indicates $\frac{2}{7}$ of the total cyanide combined with copper; on adding excess of silver nitrate, according to W. H. Virgoe [*Trans.* Inst. Min. and Met. X. 139], a further reaction occurs as follows: —

$$2KCy\cdot Cu_2Cy_2 + AgNO_3 = KAgCy_2 + Cu_2Cy_2 + KNO_3$$

When, however, potassium iodide is added, a precipitate of silver iodide occurs before any of the copper salt is decomposed, hence, none of the cyanide combined with copper is indicated in presence of KI.

Addition of water or alkali apparently renders further quantities of cyanide in the copper salt accessible to silver nitrate (in absence of KI).

Method No. 2.

Estimation of Total Cyanide by Means of Iodine in Presence of an Excess of Ferrocyanide.

As already pointed out, the indications of the iodine method of Fordos and Gélis are indistinct and unreliable for the determination

of free cyanide in presence of zinc. The total cyanide (*i.e.*, the equivalent of the cyanogen as KCy and K_2ZnCy_4, calculated as KCy) may be determined, however, with tolerable accuracy by the following modification of this method:

After removing the excess of alkali by addition of the requisite quantity of dilute acid (determined as explained above), the solution is mixed with a moderate excess of potassium ferrocyanide. On titrating the resulting mixture with a standard solution of iodine in potassium iodide, the whole of the free cyanide, together with the equivalent in KCy of all the cyanogen present in combination with zinc, is indicated, the end-point being fairly sharp and definite. In this reaction the zinc appears to be precipitated as ferrocyanide. The following equation is suggested:

$$2ZnK_2Cy_4 + K_4FeCy_6 + 8I_2 = Zn_2FeCy_6 + 8KI + 8ICy.$$

This method was found in some cases to yield very accurate results. It cannot, of course, be applied in presence of other bodies capable of reacting on iodine. (*Chemical News,* Vol. LXXII., p. 227.)

Method No. 3.

Estimation of Total Cyanide after Precipitation of the Metals with Alkaline Sulphides.

This method (*Chemical News,* Vol. LXXI., p. 274) depends on the facts: (*a*) That certain metallic cyanides, such as zinc double cyanide, K_2ZnCy_4, silver double cyanide, $KAgCy_2$, and mercuric cyanide, $HgCy_2$, are decomposed by sulphuretted hydrogen or an alkaline sulphide, with precipitation of the metal as sulphide. (*b*) That the excess of sulphide may be removed, without affecting the cyanides by the addition of insoluble compounds of lead, such as the oxides and carbonates, or soluble alkaline salts, such as the plumbates, double tartrates, etc.

In the case of zinc, the precipitation is not perfect, owing to the slight solubility of zinc sulphide in alkaline cyanides, but the result is sufficiently close for most practical purposes.

With silver the precipitation is so complete that the method might be used for the quantitative estimation of silver in cyanide solutions, cyanide being liberated (as free KCy) in exact proportion to the silver precipitated.

The copper double cyanides are generally supposed not to be decomposed by soluble sulphides, but in dilute solutions the copper is precipitated to a small extent.

The method is as follows:

The solution to be tested is mixed with a slight excess of a pure, fairly concentrated solution of sodium sulphide, well shaken, and allowed to stand until the precipitate has subsided. A little lime may be added to assist the settlement, in which case the liquid may be filtered without difficulty. A definite volume is taken; *e.g.*, if the cyanide solution originally taken measured 100 c.c., it is made up by addition of alkali solution, sodium sulphide and water to 200 c.c., and of this, 100 c.c. are removed by filtration. This portion is agitated with litharge or carbonate of lead, which is best added in small quantities at a time, with constant agitation, until a drop of the filtered liquid fulfils the following conditions:

(*a*) Does not give the slightest black or brown coloration with a drop of a solution of a lead salt. A perfectly white precipitate of lead cyanide should be produced. Lead tartrate (dissolved in alkali) gives no precipitate with cyanides. (*b*) Gives no precipitate with sodium carbonate. (*c*) Gives no precipitate with alkaline sulphides. A brown coloration may be produced, probably owing to the solution of a small quantity of the lead compound in the alkaline liquid.

When these conditions are fulfilled, a definite volume is again filtered off, say, 50 c.c., which in this case would represent 25 c.c. or one-quarter of the original cyanide solution. This is titrated with silver nitrate in the usual manner—best with addition of potassium iodide. It often happens that a slight granular precipitate is observed towards the finish, and it is necessary to add the last few drops of silver nitrate slowly, with agitation. The end-point may be made, however, perfectly definite by the addition of ammonia and potassium iodide.

It is to be particularly observed that this method indicates the cyanogen present as $KAgCy_2$ (which is not shown by titration with $AgNO_3$ with alkaline iodide indicator), in addition to free KCy and KCy as K_2ZnCy_4.

When an excess of ferrocyanide is present, the zinc is not precipitated, or only to a slight extent, by addition of sulphide; if, however, the liquid be made strongly alkaline by the addition of caustic soda, and well shaken, the zinc is almost completely converted into sulphide. In some other cases, also, the zinc fails to precipitate imme-

diately, but the precipitation generally takes place on agitation, especially if the liquid be made alkaline.

A. F. Crosse (*Journal* Chem. and Met. Soc. South Africa, Vol. III., p. 164) states that the precipitation of zinc from K_2ZnCy_4 by means of alkaline sulphides is incomplete in the cold, but practically complete at 65° C.

Experiments on the Estimation of Cyanogen in Compound Cyanides after Addition of Alkaline Sulphide.

In the following tests, known quantities of silver nitrate were added to a measured quantity of cyanide solution of known strength, then sodium sulphide added until the silver salt was partially decomposed, the mixture made up to a definite volume, filtered, and the cyanide strength determined by titration with silver nitrate.

Test No. 1.

Mixture taken.

Potassium cyanide, 1.4% KCy	50 c.c.
Silver nitrate, 1.304% $AgNO_3$	25 c.c.
Sodium sulphide, 0.27% Na_2S	5 c.c.
Water	20 c.c.
	100 c.c.

Theoretical Contents.

	Before adding sodium sulphide.	After adding sodium sulphide.
Free cyanide	0.450 gram	0.495 gram
KCy equivalent of $KAgCy_2$	0.250 gram	0.205 gram
Total cyanide	0.700 gram	0.700 gram

Results of Titration.

Volume of mixture taken. c.c.	Indicator added.	Standard $AgNO_3$ req. c.c	Free cyanide per 100 parts of mixture. Grams.
10	none	4.90	0.49
10	none	4.95	0.495 mean,
10	neutral KI	4.90	0.49 0.494
10	neutral KI	5.00	0.50

Test No. 2.

Mixture taken.

Potassium cyanide, 1.4% KCy	50 c.c.
Silver nitrate, 1.304% $AgNO_3$	25 c.c.
Sodium sulphide, 0.27% Na_2S	15 c.c.
Water	10 c.c.
	100 c.c.

Theoretical Contents.

	Before adding Na_2S Grams.	After adding Na_2S Grams.
Free cyanide	0.450	0.585
KCy equivalent of $KAgCy_2$	0.250	0.115
Total cyanide	0.700	0.700

Result of Titration.

Volume of mixture taken. c.c.	Indicator added.	$AgNO_3$ standard sol. required. c.c.	Free cyanide indicated per 100 c.c. of mixture. Grams.
10	None	5.85	0.585
10	KI	5.80	0.580
10	KI	5.85	0.585

Test No. 3.

Mixture taken.

Potassium cyanide, 1.4% KCy	50 c.c.
Silver nitrate, 1.304% $AgNO_3$	25 c.c.
Sodium sulphide, 0.27% Na_2S	25 c.c.
	100 c.c.

Theoretical Contents.

	Before adding Na_2S Grams.	After adding Na_2S Grams.
Free cyanide	0.450	0.675
KCy equivalent of $KAgCy_2$	0.250	0.025
Total cyanide	0.700	0.700

Result of Titration.

Volume of mixture taken. c.c.	Indicator added.	Standard $AgNO_3$ required. c.c.	Free cyanide indicated per 100 c.c. of mixture. Grams.
10	None	6.75	0.675
10	KI	6.80	0.680
10	KI	6.70	0.670

In the three tests above, the following reactions are assumed:

(1) $2KCy + AgNO_3 = KAgCy_2 + KNO_3$.

(2) $2KAgCy_2 + Na_2S = Ag_2S + 2KCy + 2NaCy$.

In the following tests, to which zinc as well as silver was added, it is assumed that the following reaction occurs after the completion of reaction (2) when sufficient Na_2S has been added:

(3) $K_2ZnCy_4 + Na_2S = ZnS + 2KCy + 2NaCy$.

On titrating the resulting solution with $AgNO_3$, after making strongly alkaline and adding KI, all the cyanogen existing as KCy, NaCy or K_2ZnCy_4 should be indicated as its equivalent of KCy.

TEST NO. 4.

Mixture taken.

Potassium cyanide, 1.4% KCy	50 c.c.
Zinc sulphate, 1% Zn	10 c.c.
Silver nitrate, 1.304%, $AgNO_3$	15 c.c.
Sodium sulphide, 0.33% Na_2S	10 c.c.
Water	15 c.c.
	100 c.c.

Theoretical Contents.

	Before adding Na_2S Grams.	After adding Na_2S Grams.
Free cyanide	0.15	0.26 } 0.66
KCY equivalent of K_2ZnCy_4	0.40	0.40 }
KCy equivalent of $KAgCy_2$	0.15	0.04
Total cyanide	0.70	0.70

Result of Titration.

Volume of solution tested.	Cyanide indicated per 100 parts of mixture.		
	Without KI Grams.	With neutral KI Grams.	With alkaline KI Grams.
10 c.c. in each case.	0.37	0.495	0.655
	.....	0.50	0.660
	.....	.....	0.655

TEST NO. 5.

Mixture taken.

Potassium cyanide, 1.23% KCy	50 c.c.
Zinc sulphate, 1% Zn	10 c.c.
Silver nitrate, 1.304% $AgNO_3$	20 c.c.
Sodium sulphide, 0.33% Na_2S	10 c.c.
Water	10 c.c.
	100 c.c.

Theoretical Contents.

	Before adding Na_2S Grams.	After adding Na_2S Grams.
Free cyanide	0.015	0.125 } 0.525
KCy equivalent of K_2ZnCy_4	0.400	0.400 }
KCy equivalent of $KAgCy_2$	0.200	0.090
Total cyanide	0.615	0.615

Result of Titration.

Volume of mixture taken,	Cyanide indicated per 100 parts of mixture.		
	Without KI Grams.	With neutral KI Grams.	With alkaline KI Grams.
10 c.c. in each case.	0.27	0.385	0.525 0.525

TEST NO. 6.

Mixture taken.

Potassium cyanide, 0.54% KCy	25 c.c.
Sodium zincate, 0.1% Zn	20 c.c.
Sodium sulphide, 0.156% Na_2S	20 c.c.
Water	35 c.c.
	100 c.c.

Theoretical Contents.

	Before adding Na_2S Grams.	After adding Na_2S Grams.
Free cyanide	0.055	0.135
KCy equiv. of K_2ZnCy_4	0.080	.....
Total cyanide	0.135	0.135

Solution treated with lime and filtered, then treated with lead carbonate and filtered again.

Result of Titration.

Volume of filtrate taken for test. c.c.	Volume of $AgNO_3$ required with alkaline KI as indicator. c.c.*	Cyanide indicated per 100 parts of mixture. Grams.
50	12.9	0.129
40	10.4	0.130

* 1 c.c. $AgNO_3$ solution=0.005 gram KCy.

Test No. 7.

A solution was prepared having the following theoretical composition:

Free cyanide, KCy	0.2%
KCy equivalent of K_2ZnCy_4	0.2%
Total cyanide (as KCy)	0.4%
Ferrocyanide (as $K_4FeCy_6 \cdot 3H_2O$)	0.2%
Thiocyanate (as KCyS)	0.04%
Bicarbonate (as $NaHCO_3$)	0.39%
Carbonate (as Na_2CO_3)	0.06%
Chloride (as NH_4Cl)	0.1%

The zinc was added in the form of zinc sulphate (solution containing 0.5 per cent Zn).

(*a*) Test for total cyanide by direct titration with silver nitrate, using alkaline iodide indicator, showed 0.4 per cent KCy.

(*b*) Tests were made by taking 50 c.c. of the above mixture, and adding excess of sodium sulphide. No precipitate of zinc sulphide occurred until the liquid was made strongly alkaline by adding lime and agitating.

The mixture was made up to 100 c.c., filtered, the filtrate agitated with 1 gram of lead carbonate, and again filtered, then tested with $AgNO_3$ and alkaline iodide indicator.

Volume of original solution taken. c.c.	Volume of filtrate tested. c.c.	Fraction of original solution.	Volume of $AgNO_3$ required. c.c.	Amount of KCy indicated. %
50	90	9/10	34.20	0.380
50	90	9/10	33.95	0.377

See Appendix, page 161.

SECTION 3.

Estimation of Total Cyanogen.

The term total cyanogen will be used to indicate all the cyanogen present in the solution, whether in the form of simple cyanides, double cyanides, hydrocyanic acid or compounds such as ferro- and

ferricyanides, sulphocyanides, cyanates and isocyanates. Some of the methods here described are not actually universal, but the substances excepted (of which the cyanogen cannot be determined by the process in question) are of unusual occurrence in practice.

The methods detailed below are:

1. The volumetric method of Vielhaber, by titrating with silver nitrate and potassium chromate indicator.
2. Gravimetric method with silver nitrate and nitric acid.
3. Gravimetric method with silver nitrate and ammonia.
4. Gravimetric method with oxide of mercury.
5. The total cyanogen may also be determined by estimating the carbon and nitrogen obtained in the ultimate analysis of the compounds by the methods of organic analysis, for which reference must be made to works on that subject.

Method No. 1.

Estimation of Total Cyanogen by Titration with Silver Nitrate, Using the Chromate Indicator.

This process, described by Veilhaber (*Arch. Pharm.* [3], XIII, 408), is merely an adaptation of the ordinary volumetric method of estimating chlorides devised by Mohr. Chlorides are, of course, estimated along with the cyanogen compounds, and when present must be separately determined.

The method is as follows:

Two or three drops of a saturated solution of neutral (yellow) potassium chromate, K_2CrO_4, are added to the solution to be titrated, and the standard silver solution run in until a faint reddish tinge appears and remains permanent on shaking. With a pure solution of a simple cyanide, twice as much silver nitrate solution must be added as in Liebig's method, in order to obtain the reaction, since the indication with chromate does not occur until the whole of the cyanide has been precipitated, as follows:

(*a*) $2KCy + AgNO_3 = KAgCy_2 + KNO_3$,

(*b*) $KAgCy_2 + AgNO_3 = 2AgCy + KNO_3$;

after which (in the absence of chlorides and other cyanogen compounds) red silver chromate is precipitated as follows:

(*c*) $K_2CrO_4 + 2AgNO_3 = Ag_2CrO_4 + 2KNO_3$.

The solution must not contain any considerable amount of free alkali. If this be present, it must be first neutralized by the addition

of the requisite amount of dilute sulphuric or nitric acid (not hydrochloric acid), which may be determined as already described.

When hydrocyanic acid is present Vielhaber recommends neutralizing with magnesium carbonate suspended in water.

The reactions with commonly-occurring substances precipitable by silver nitrate in a cyanide solution, occur more or less in the following order, all these reactions being completed before the chromate color becomes permanent:

(1) $2KCy + AgNO_3 = KAgCy_2 + KNO_3$.
(2) $KAgCy_2 + AgNO_3 = 2AgCy + KNO_3$.
(3) $KCl + AgNO_3 = AgCl + KNO_3$.
(4) $KSCy + AgNO_3 = AgSCy + KNO_3$.
(5) $K_4FeCy_6 + 4AgNO_3 = Ag_4FeCy_6 + 4KNO_3$.
(6) $K_2ZnCy_4 + AgNO_3 = ZnCy_2 + KAgCy_2 + KNO_3$.
$ZnCy_2 + 2AgNO_3 = Zn(NO_3)_2 + 2AgCy$.

The reactions taking place with zinc double cyanides on the addition of silver nitrate in presence of an excess of ferrocyanide are discussed by L. M. Green in a paper laid before the Institute of Mining and Metallurgy, October 17, 1901 (*Proceedings,* Vol. X., p. 29).

Isocyanates, if present, will also be precipitated by silver nitrate before the chromate reaction is obtained. Cyanates and bicarbonates are apparently not precipitated. Carbonates obscure the finishing point somewhat (acting probably in the same way as caustic alkalis), but the chromate reaction occurs before the carbonate has been precipitated by silver as Ag_2CO_3.

Chloride of silver may be separated from the cyanide by boiling with concentrated nitric acid, which decomposes the cyanide but leaves the chloride undissolved.

Method No. 2.

Gravimetric Determination of Total Cyanogen by Means of Silver Nitrate and Nitric Acid.

Fresenius (*Quant. Anal.,* 7th ed., Vol. I., p. 375) describes the following method, due to H. Rose:

"Digest for some time with a dilute solution of nitrate of silver, stirring frequently, then add nitric acid in moderate excess, and digest at a gentle heat, till the foreign cyanide is fully dissolved

and the cyanide of silver has become pure and white. (Double cyanide of nickel and potassium yields by this process a mixture of cyanide of silver with cyanide of nickel. Like double cyanides are similarly decomposed.) Then add water and filter. As a precautionary measure it is well to test the metal obtained by long ignition of the cyanide of silver, whether it is free from those metals which were combined with the cyanogen. The filtrate is used for estimating the bases, the silver being first precipitated with hydrochloric acid. This method affords an exact analysis of the double cyanides of potassium with nickel, copper and zinc."

I may here remark that I have used a practically identical method, with good results, for the estimation of copper in cyanide solutions, the copper being determined in the filtrate by a colorimetric method.

The precipitated cyanide of silver may be collected on a weighed filter, dried at 100° and weighed, or it may be collected on an unweighed filter and converted into metallic silver by igniting in a porcelain crucible for a quarter of an hour, or until it ceases to lose weight.

The following remarks (Fresenius, *Quant. Anal.,* 7th ed., Vol., I., p. 141) on the properties of cyanide of silver may be of use in this connection: "Cyanide of silver may be dried at 100° without decomposition; it is soluble in ammonia. Exposure to light fails to impart the slightest tinge of black to it. Upon ignition it is decomposed into cyanogen, which escapes, and metallic silver, which remains mixed with a little paracyanide of silver. By boiling with a mixture of equal parts of sulphuric acid and water, it is, according to Glassford and Napier, dissolved to sulphate of silver, with liberation of hydrocyanic acid."

It is to be observed that this method of precipitation with silver nitrate in presence of excess of nitric acid cannot conveniently be employed in presence of ferrocyanides, as they yield a precipitate of silver ferrocyanide and not of AgCy, and on ignition this leaves some oxide of iron, together with metallic silver. Chlorides also interfere; chloride of silver is formed, which does not decompose on ignition for one-quarter hour at a moderate temperature.

When thiocyanates are present in the original liquid the precipitate will contain silver thiocyanate, which on ignition will yield metallic silver proportional to the cyanogen.

From these considerations it will be seen that in dealing with

impure solutions, the method is more useful as a means of eliminating cyanogen as a preliminary step for other determinations than as a means of determining cyanogen itself.

Method No. 3.

Gravimetric Determination of Total Cyanogen by Means of Silver Nitrate and Ammonia.

W. Weith (*Zeitschrift f. analyt. Chem.*, 9, 379) recommends a solution of nitrate of silver in ammonia for the decomposition of many cyanogen compounds, such as ferrocyanide of potassium, Prussian blue, and even cobalticyanide of potassium. He digests them in sealed tubes at 100° C. (in the case of cobalticyanide of potassium at 150° C.) for 4 or 5 hours. The contents of the tube are then gently warmed in a dish until the crystals of ammonio-cyanide of silver are dissolved. Any separated metallic oxide is filtered off and washed with ammonia. The filtrate is diluted, and cyanide of silver precipitated therefrom by acidifying with nitric acid. This may be collected and determined as in the previous method. The method would probably be chiefly applicable to the solid cyanogen compounds, rather than to solutions.

In the filtrate the silver may be separated from the alkalis, etc. In respect to the undissolved oxides, it should be noted that metallic silver is always mixed with the oxide of iron.

Method No. 4.

Gravimetric Determination of Total Cyanogen by Boiling with Oxide of Mercury.

The following account of this method is given by Fresenius (*Quant. Anal.*, 7th ed., Vol. I., p. 376):

"Many simple cyanides, and also double cyanides, both of the character of the double cyanide of nickel and potassium and of the ferro- and ferricyanide (not, however, cobalticyanides) may, as is well known, be completely decomposed by boiling with excess of oxide of mercury and water, all cyanogen being determined as cyanide of mercury and the metals passing into oxides."

H. Rose has shown that Prussian blue, ferro- and ferricyanide of

potassium, more particularly, may be readily analyzed in this manner:

"Boil a few minutes with water and excess of oxide of mercury until complete decomposition is effected, and, in order to render the sesquioxide of iron and oxide of mercury removable by the filter, nitric acid in small portions, till the alkaline reaction has nearly disappeared, filter, wash with hot water, dry the precipitate, ignite, very gradually raising the heat under a hood with a good draught, and weigh the sesquioxide of iron remaining."

The cyanogen is determined in the filtrate as follows:

"Mix the solution (containing the cyanogen as cyanide of mercury) with nitrate of zinc dissolved in ammonia. To one part of mercury salt add about two parts of the zinc salt. Add to the clear solution sulphuretted hydrogen water gradually till it produces a perfectly white precipitate of sulphide of zinc. The precipitate, which is a mixture of the sulphides of mercury and zinc, settles well. After a quarter of an hour filter it off and wash with very dilute ammonia. The filtrate contains cyanide of zinc dissolved in ammonia, together with nitrate of ammonia. It does not smell of hydrocyanic acid, and consequently no escape of the latter takes place. Mix it with nitrate of silver and then add dilute sulphuric acid in excess. The cyanide of silver is next washed a little by decantation, then—to free it from any cyanide of zinc simultaneously precipitated—heated with a solution of nitrate of silver, finally filtered off, washed and weighed, after drying at 100°, as AgCy or (after ignition) as metallic silver."

The cyanogen in the filtrate from the precipitate of mixed sulphides could, of course, be determined volumetrically by titration with silver nitrate and potassium iodide indicator.

See Appendix, page 163.

SECTION 4.

Estimation of Hydrocyanic Acid.

Free hydrocyanic acid may be estimated by titration with silver nitrate

(*a*) After addition of an excess of caustic alkali.

(*b*) After addition of an excess of bicarbonate.

Detection of hydrocyanic acid:

The presence of any considerable quantity of hydrocyanic acid in

a solution may be detected by its smell, or by covering a beaker containing a little of the solution with a watch-glass, on the under surface of which is a drop of silver nitrate. If the drop rapidly becomes milky, the presence of hydrocyanic acid is indicated.

Solutions containing the free acid are best measured by means of a graduated column. If a pipette be used a plug of cotton wool slightly moistened with silver nitrate should be inserted into the upper end, to avoid the danger of inhaling the acid.

Method No. 1.

Estimation of Hydrocyanic Acid by Silver Nitrate with Addition of Alkali.

This modification of Liebig's method, suggested originally by Siebold, is described by Sutton (*Volum. Anal.*, 8th ed., p. 217). The liquid to be titrated is measured from a burette dipping into a solution of caustic alkali contained in a beaker. The resulting alkaline cyanide is then titrated with silver nitrate in the ordinary way. A large excess of alkali must be avoided, unless the potassium iodide indicator be used.

If the original solution also contains free cyanide, *i.e.*, cyanides of the alkali or alkaline earth metals, a separate determination must be made by titrating with silver nitrate without adding caustic alkali; the result of this titration, deducted from that of the first, gives the equivalent in terms of KCy of the hydrocyanic acid present. It may here be remarked that the finishing point in presence of free hydrocyanic acid is somewhat indefinite.

This method is, of course, not applicable in presence of easily decomposed double cyanides, such as K_2ZnCy_4, as these would be determined along with the cyanide resulting from the HCy, after addition of alkali. Ferrocyanides and sulphocyanides should not interfere.

Method No. 2.

Estimation of Hydrocyanic Acid by Silver Nitrate after Adding an Alkaline Bicarbonate.

This method, described by Bettel (*Proceedings* Chem., Met. Soc. South Africa, Vol. I., p. 165), is said to be applicable in presence of double cyanides such as K_2ZnCy_4.

The free cyanide is first estimated in the ordinary way, without addition of alkali.

Another portion of the liquid is then taken, and a solution of potassium or sodium bicarbonate free from monocarbonate is added. Free carbonic acid must be absent. The resulting liquid is then titrated with silver, and the result of the first titration deducted from the number found. This gives the equivalent in KCy of the hydrocyanic acid present.

The method depends on the reaction:

$$2KHCO_3 + AgNO_3 + 2HCy = KAgCy_2 + KNO_3 + 2CO_2 + 2H_2O,$$

and is therefore a reversal of Siebold's method of estimating carbonates by means of hydrocyanic acid and silver nitrate. (*Year Book of Pharmacy,* 1878, p. 518.) Bicarbonates have no action on potassium or sodic zinc cyanide.

Instead of silver nitrate, an iodine solution could presumably be used where interfering substances are absent, the reaction being

$$KHCO_3 + I_2 + HCy = KI + ICy + CO_2 + H_2O.$$

SECTION 5.

Estimation of Available Cyanide.

The efficiency of a cyanide solution for dissolving gold and silver depends on various other factors besides the percentage of cyanogen in the form of simple cyanides. The amount of precious metal dissolved in any particular case will be determined by the following considerations: (*a*) Time of contact. (*b*) Quantity of solution in proportion to metal to be dissolved. (*c*) Temperature. (*d*) Physical condition of the metal acted upon. (*e*) Nature of surrounding bodies; for example, the presence or absence of other substances which might be attacked by cyanide. (*f*) Amount and nature of other salts in solution, some of which may either assist or hinder the action of cyanide, or may be themselves solvents or precipitants of the precious metals. (*g*) Amount of dissolved oxygen in the solution. (*h*) Size or shape of the containing vessel —this being chiefly of importance in view of the admission or exclusion of air. (*i*) Mode of application of the solution, *e.g.,* by percolation, agitation, etc.

It has been shown that the double cyanide of zinc and potassium is to some extent a solvent of gold, though much less efficient than a simple cyanide, for equal quantities of cyanogen.

Ferro- and ferricyanides may also act directly in some instances. Hydrocyanic acid is also a possible solvent. In some of these cases, particularly that of K_2ZnCy_4, it is not very clear whether the action may not be due (as suggested by T. K. Rose, *Metallurgy of Gold,* p. 398) to dissociation of the compound with liberation of free cyanide. Careful experiments (*Proceedings* Inst. Min. & Met., Vol. VI., p. 120) appear to have proved that cyanogen is not a solvent of gold.

The researches of Maclaurin (*Journal* Chem. Soc., Vol. LXVII.) and others have demonstrated that the efficiency of pure solutions depends on the amount of dissolved oxygen as well as upon the percentage of cyanide, and, in fact, that when solutions of various strengths are compared under otherwise similar conditions, there is a certain strength which shows a maximum efficiency. Thus a solution of 0.25 per cent was found to dissolve gold and silver more rapidly than any other, either stronger or weaker. This result appears to be due to the fact that the solubility of oxygen in cyanide solutions diminishes as the percentage of cyanide is increased, so that the conditions most favorable for the occurrence of the reactions

$$4KCy + 2Au + O + H_2O = 2KAuCy_2 + 2KOH,$$
$$4KCy + 2Ag + O + H_2O = 2KAuCy_2 + 2KOH,$$

are obtained with this particular degree of concentration. Between the limits 0.1 per cent and 0.25 per cent the efficiency was found to be nearly constant. It is obvious, therefore, that a mere determination of free cyanide gives us no information as to the efficiency of a solution unless other circumstances are taken into consideration, for a 1 per cent solution might have actually less efficiency than a 0.1 per cent solution.

In many cases some method of rapidly and accurately estimating the solvent power of a solution (under given conditions) would be of the utmost value. Unfortunately no thoroughly reliable method exists, and we are practically obliged to fall back upon comparative extraction tests which really amount to an experimental treatment of the ore or material under examination, in which actual working conditions are imitated as closely as possible.

Several methods have, however, been tried by different experi-

menters, depending on the rate of solution of small quantities of metal in the liquid to be examined, and some description of these will be given below.

The term 'available cyanide' (or perhaps better 'solvent activity') might be defined as follows:

"Two solutions are said to have the same solvent activity when equal volumes dissolve the same amounts of precious metal in the same time and under the same conditions." If we take a certain solution for a standard (say, for example, a 0.25 per cent solution of pure potassium cyanide in well aërated distilled water), we might represent the weight of gold dissolved by the standard solution as 100, and that dissolved by some other solution might then be expressed in terms of a percentage of this standard. Thus if w_1 and w_0 be the weights dissolved by a given solution and the standard respectively, then the solvent activity of the given solution would be expressed by $100 \times (w_1 \div w_0)$.

It is obvious that the term can only be used in reference to a particular set of conditions, and that comparisons can only be made where all essential points are the same in all tests.

Descriptions of experimental treatment tests hardly come within the scope of a paper on the 'analysis of cyanide solutions'; for these reference may be made to various works on the cyanide process.

Method for the Estimation of Available Cyanide by the Rate of Solution of Metallic Gold or Silver.

Tests made by immersing weighed pieces of gold and silver foil for equal intervals of time, respectively, in the solution to be tested and in standard solutions of different strengths, and determining the loss of weight in each case, gave varied and discordant results (J. S. Maclaurin, *Journal* Chem. Soc., Vol. LXVII., p. 199), as it is practically impossible to secure uniform conditions. Moreover, such results could not be safely applied in estimating the relative efficiency of solutions for another purpose (as, for example, for the treatment of some particular ore).

I have recently experimented on a method of comparing the solvent activity of solutions capable of giving results which may be of some value, with comparatively little trouble, and in a reasonably short time. Six or more tests might be executed simultaneously in about an hour.

A solution of chloride of gold is prepared by dissolving pure metallic gold in aqua regia, evaporating to dryness on a water bath, and dissolving in pure water to a definite volume. A solution containing 0.5 milligram Au per c.c. is a convenient strength. A number of exactly similar flasks are got ready, and an equal volume (say 10 c.c.) of the gold chloride solution added to each. A few drops of a concentrated solution of sulphur dioxide in distilled water is added to each flask, and the liquid then boiled till there is no smell of SO_2. The whole of the gold will be thus precipitated in a fine powder, and the conditions in each flask will be as nearly as possible identical. Add to each a few c.c. of a N/10 solution of sodium hydrate, so that the liquid in the flasks becomes faintly alkaline. Cool, and then add to the flasks equal volumes of the various solutions to be compared (at least two tests should be made with distilled water). The flasks are then agitated at intervals for 15 minutes, and the residual gold collected on filters, and washed once or twice with distilled water until the washings are free from cyanide. The filter papers are dried in porcelain dishes on a sand bath (or in any other convenient way), wrapped in lead foil and cupelled. The resulting gold beads are weighed, and the solvent activity obtained by calculation. The amount of gold dissolved is equal to the weight of bead from test with distilled water, less the weight of bead from test with given solution. This method introduces no foreign bodies except small quantities of alkaline chlorides and sulphates and of sodium hydrate, which are quite inactive, and are, moreover, practically present in equal amount in all the tests.

See Appendix, page 164.

CLASS II.

ALKALINE CONSTITUENTS.

General Remarks on the Action of Different Indicators toward Substances found in Cyanide Solutions.

Before proceeding to discuss the methods of estimating the alkalinity of working cyanide solutions, it is necessary to point out the behavior of different indicators toward the various bodies likely to be found in such solutions.

The estimation of alkalinity is generally made by means of a dilute standard solution of some mineral acid (H_2SO_4, HCl or HNO_3). Sometimes an organic acid (for example, oxalic acid) may be used. The indicators most commonly employed are litmus, phenol phthaleïn and methyl orange, and these alone will be considered in the following remarks. The methods of preparing these indicators and their general characteristics are fully described by Sutton (*Volum. Anal.*, 8th ed., p. 33).

Methyl orange should not be used when organic acids are employed for the titration. A convenient strength is 0.1 per cent, in aqueous solution, a single drop being generally sufficient for each test. The tint is then very pale yellow in alkaline or neutral solutions and pink in acid.

Phenol phthaleïn is used in the form of an alcoholic solution (in methylated spirit or 60 per cent alcohol). About 0.5 per cent is a convenient strength. The tint is deep pink (rose color) in alkaline and colorless in acid or neutral solution.

1. *Action Toward Simple Cyanides.* — Free potassium cyanide and other cyanides of the alkali metals behave, when neutralized by dilute mineral acids (and some organic acids), as if the whole of the alkali metal existed in the form of hydrate. When methyl orange is used as the indicator the end-point is fairly sharp; with litmus and phenol phthaleïn it is somewhat indefinite, as these indicators are affected by the hydrocyanic acid evolved, but with care the amount of standard acid required will be found to correspond pretty closely, whatever indicator be used, to the completion of the reaction:

$$KCy + HR = HCy + KR,$$

or its equivalent, R being any monovalent acid radicle.

2. *Action Toward Alkaline Hydrates.*—Alkaline hydrates (*e.g.*, caustic potash, KOH, caustic soda, NaOH, lime, $Ca(OH)_2$, etc.) are alkaline to all indicators, the amount of standard acid used corresponding to the total amount of the alkali metal present and indicating the completion of the reaction:

$$MOH + HR = H_2O + MR, \text{ where}$$

M = any positive monovalent radicle or its equivalent, and
R = any negative monovalent radicle or its equivalent.

3. *Action Toward Alkaline Monocarbonates.* — These (*e.g.*, Na_2CO_3, K_2CO_3) are also alkaline to the mineral acids (HCl, HNO_3, H_2SO_4), and some organic acids, but the amount of acid required to effect the change in the indicator depends on the nature of the indicator used.

With *methyl orange* the whole of the alkali metal is indicated as though it were present as hydrate, the permanent pink tint only appearing after the completion of the reaction:

$$K_2CO_3 + 2HR = H_2O + CO_2 + 2KR,$$

or its equivalent.

With *litmus* the reaction in the cold is always incomplete, owing to the action of the liberated carbonic acid on the indicator. If the titration be performed with the solution to be examined at boiling temperature, the whole of the alkali metal of the carbonate may be estimated.

With *phenol phthaleïn* the finishing point is also somewhat indefinite owing to the same cause, but it is possible to estimate by means of this indicator, with tolerable accuracy, the amount of monocarbonate in dilute solutions, the finishing point being the same as though half the alkali metal of the carbonate existed in the form of hydrate, thus corresponding with the completion of the reaction:

$$K_2CO_3 + HR = KHCO_3 + KR,$$

or its equivalent.

Ammonium carbonate behaves in a similar manner, but the end point with phenol phthaleïn is uncertain, owing to free ammonia present in the solution.

4. *Action Toward Bicarbonates.*—The bicarbonates of the alkali and alkaline earth metals ($NaHCO_3$, $KHCO_3$, $CaH_2(CO_3)_2$) are neutral to phenol phthaleïn and to litmus, but alkaline to methyl orange, the whole of the alkali metal being indicated as though present as hydrate according to the equation:

$$KHCO_3 + HR = H_2O + CO_2 + KR,$$

or its equivalent.

5. *Action Toward Ammonia.*—Ammonia is alkaline to all indicators, but cannot be accurately titrated with phenol phthaleïn.

6. *Action Toward Zinc Double Cyanides.*—The double cyanide of zinc and potassium behaves, when titrated with standard acid, using methyl orange as indicator, as though the whole of the cyanogen existed as free potassium cyanide, the finishing point indicating the completion of the reaction:

$$K_2ZnCy_4 + 4HR = ZnR_2 + 2KR + 4HCy.$$

[With phenol phthaleïn the alkalinity obtained varies according to the degree of dilution and probably represents the cyanide liberated from that portion of the double salt which has become dissociated according to the reaction:

$$K_2ZnCy_4 \rightleftharpoons ZnCy_2 + 2KCy.]$$

7. *Action Toward Alkaline Zincates.*—Potassium zincate, $Zn(OK)_2$, behaves to methyl orange and phenol phthalein as though the alkali metal existed entirely as hydrate.

8. *Action Toward Alkaline Sulphides.*—The sulphides of the alkali metals (K_2S, Na_2S, presumably, also, CaS, BaS and similar bodies) react towards acids with methyl orange indicator as though the alkali metal existed as hydrate:

$$K_2S + 2HR = 2KR + H_2S.$$

With phenol phthaleïn in a cold solution, the neutral point indicates half the alkali metal present:

$$K_2S + HR = KHS + KR.$$

With boiling solutions the reaction is the same as with methyl orange.

The effects are thus precisely analogous to those obtained with monocarbonates.

9. The following substances are neutral to all indicators:
Double cyanides of silver ($KAgCy_2$, $NaAgCy_2$).

Ferrocyanides,
Ferricyanides,
Sulphocyanides,
Chlorides,*
Sulphates,
Nitrates,
} when present as normal salts of the alkali or alkaline earth metals.

* Including ammonium chloride.

From the foregoing remarks it will be seen that, of the three indicators, methyl orange is the most sensitive to alkalis, and phenol phthaleïn the most sensitive to acids. By a combination of tests with these two indicators we may sometimes determine several different ingredients in the solution.

Definition of 'Total' and 'Protective' Alkali.—The 'total alkali' of a solution will be defined as the equivalent, in terms of caustic potash (KOH), of all the ingredients which are alkaline to methyl orange. It is, therefore, the sum of the alkalinities due to the several substances which are alkaline to this indicator. The chief of these are:

Simple cyanides,
Hydrates,
Carbonates,
Bicarbonates,
Sulphides,
Zincates,
} of the alkali and alkaline earth metals Na, K, NH_4, Ca, Ba, etc.
Double cyanides of zinc,
Free ammonia,

The term 'protective alkali' is based on the assumption that certain ingredients in an ordinary working solution will be wholly or partially neutralized, on addition of a dilute mineral acid, or carbonic acid, before any decomposition of cyanide occurs. In the treatment of ores the addition of lime or caustic soda is made with the object of protecting the cyanide from the decomposing effect of various matters contained in the ore, and of the carbonic acid in the air. As a matter of fact, a cyanide solution undergoes gradual decomposition, with evolution of hydrocyanic acid, even when an excess of caustic alkali is present, so that the protection afforded is only partial and temporary, and not absolute. There is, however, a fairly definite point in the neutralization of an ordinary solution (containing free cyanide, hydrates, carbonates, etc.) at which the decomposition, with formation of hydrocyanic acid, begins to take place with marked rapidity. In the absence of zinc this point corresponds with tolerable exactness to the alkalinity of the hydrates and carbonates present toward phenol phthaleïn, and if the amount of acid corresponding to this alkalinity be added, with agitation, to such a solution, the cyanide strength, as shown by *immediate* titration with silver nitrate, will remain apparently unchanged. In this case, therefore, protective alkali = hydrate + ½ carbonate.

When zinc is present the effect of adding dilute acid is somewhat remarkable, and has been referred to in detail in the discussion on Mr. L. M. Green's paper on the 'Titration of Cyanide Solutions Containing Zinc.' No loss of cyanogen (and hence no evolution of HCy) takes place even on prolonged exposure, unless the acid added exceeds a certain amount.

The various determinations of alkaline constituents here considered will be as follows:

(*A*) *Total Alkali.*—Titration by standard acid and methyl orange indicator.

(*B*) *Protective Alkali.*—(1) Titration with standard acid and phenol phthaleïn after adding silver nitrate.

2. Titration with the same, after adding excess of potassium ferrocyanide.

3. Distillation with potassium bisulphate.

(*C*) *Hydrates.*—(1) By combined titrations with standard acid and the two indicators, making the necessary corrections for cyanides and carbonates.

2. By titration with standard acid after precipitation of the cyanide with $AgNO_3$ and the carbonate with $BaCl_2$.

(*D*) *Carbonates and Bicarbonates.*—(1) By calculation from results of the preceding tests.

2. By precipitation as $BaCO_3$ and estimation of the CO_2 corresponding to precipitate found.

(*E*) *Ammonia* (*and Ammonium Salts*).—By colorimetric test with Nessler's solution after precipitation of cyanogen compounds and distillation of the filtrate.

(A) Estimation of Total Alkali.

A measured volume (say 50 c.c.) of the solution is placed in a flask with a few drops of a 0.1 per cent solution of methyl orange. N/10 acid (HCl, HNO_3 or H_2SO_4) is run in from a burette until a faint permanent pink tint is produced.

When the solution contains double cyanides of zinc, copper, silver, etc., a white precipitate occurs at a certain stage on the addition of acid, consisting of the simple cyanides of these metals. As this precipitate obscures the finishing point of the reaction with methyl orange, it is perhaps better, in such cases, to add an excess of the standard acid, that is to say, to continue adding acid until no further

precipitation takes place, and determine the excess of acid in the filtrate, or a definite fraction of it, by titration with standard alkali.

In this case, however, the whole of the alkali metal of the double salts will be determined as forming part of the total alkali, the probable reactions being

$$K_2ZnCy_4 + 2HR = ZnCy_2 + 2HCy + 2KR,$$
$$K_2Cu_2Cy_4 + 2HR = Cu_2Cy_2 + 2HCy + 2KR,$$
$$KAgCy_2 + HR = AgCy + HCy + KR,$$

R being any negative monovalent radicle,

(B) Estimation of Protective Alkali.

Method No. 1.

Titration with Standard Acid and Phenol Phthaleïn Indicator, after Addition of Silver Nitrate.

This method was devised by the writer in 1894, and is fully described in the *Chemical News,* Vol. LXXI., p. 93. It is based on the facts already pointed out: (*a*) That double cyanides of silver are neutral to phenol phthaleïn. (*b*) That the amount of acid required to neutralize the hydrates and carbonates towards phenol phthaleïn is a measure of protective alkali as defined. (*c*) That the presence of cyanide or double cyanide of silver does not interfere with the titration of alkali, the double salt not being decomposed until the whole of the alkali is neutralized.

The principal substances included in this test are: Hydrates, carbonates (converted in the titration to bicarbonates), ammonia, a small portion of K_2ZnCy_4, zincates ($Zn(OK)_2$). The latter probably do not coexist with free cyanides.

The method of testing is as follows: Silver nitrate is added to a measured volume of the solution until a permanent turbidity is produced. The ordinary standard solution may be used, so that the same measured portion of the liquid to be tested will serve for the determination of both cyanide and protective alkali. This latter is a great advantage of the method in practical work, and enables it to be applied constantly for the control of daily operations in the cyanide plant, the test being so simple as to be well within the capacity of the "average man on shift." Addition of even a considerable quantity of silver in excess of the necessary amount does not materially affect the result. A drop of the alcoholic 0.5 per cent phenol phthaleïn solution is now added to the turbid liquid in the flask (without filtering), and the resulting pink fluid is titrated

with N/10, or any convenient standard acid, until the color entirely disappears. The amount of standard acid used measures the protective alkali.

Influence of Zinc.—As already pointed out, only a small portion of K_2ZnCy_4 is shown as alkali when titrated with acid and phenol phthaleïn. Moreover, the addition of excess of silver nitrate after the first turbidity causes the K_2ZnCy_4 solution to become quite neutral to this indicator at some point before the complete precipitation of the cyanide. When large quantities of zinc are present (in absence of much hydrate or carbonate of the alkalis), addition of silver nitrate, as recently pointed out by L. M. Green, causes the solution to become acid to phenol phthaleïn. (See App., p. 167.)

Method No. 2.

Estimation of Protective Alkali after Addition of Silver Nitrate and Potassium Ferrocyanide.

The following method, devised by Leonard M. Green (*Proceedings* Inst. Min. and Met., October, 1901), obviates the difficulties in the last method due to the presence of zinc, but it is questionable whether the value obtained represents the protective alkali as defined. (See p. 61 above.)

The method is, briefly, as follows: The total cyanide is first determined by titration with silver nitrate, using the alkaline iodide indicator. Another portion, say, 50 c.c., of the original solution is now taken, an excess of ferrocyanide solution added, and then a little more silver solution than was used in the previous test, to ensure the complete conversion of all cyanides into silver salts. Phenol phthaleïn is then added and the liquid titrated with standard acid as in the previous method. We may suppose the reactions (in absence of alkalis and ferrocyanides) to be as follows, while zinc double cyanide is in excess:

(*a*) $K_2ZnCy_4 + AgNO_3 = ZnCy_2 + KAgCy_2 + KNO_3$;

but in presence of a sufficient excess of silver nitrate,

(*b*) $K_2ZnCy_4 + 2AgNO_3 = 2KAgCy_2 + Zn(NO_3)_2$.

Bettel (*Journal* Chem. and Met. Soc. South Africa, Vol. I., p. 164) gives the following as the reaction taking place when excess of ferrocyanide is added to a solution of the zinc double cyanide:

$$3K_2ZnCy_4 + 2K_4FeCy_6 = K_2Zn_3(FeCy_6) + 12KCy,$$

so that in presence of an excess of $AgNO_3$ the solution would become neutral by conversion of KCy into $KAgCy_2$.

In absence of ferrocyanide the acidity to phenol phthaleïn may be due to the presence of zinc nitrate, which would neutralize any alkaline hydrate or carbonate as follows:

$$Zn(NO_3)_2 + 2KOH = Zn(OH)_2 + 2KNO_3,$$
$$Zn(NO_3)_2 + K_2CO_3 = ZnCO_3 + 2KNO_3.$$

On addition of ferrocyanide the alkali is regenerated as follows:

$$K_4FeCy_6 + Zn(OH)_2 = ZnK_2FeCy_6 + 2KOH,$$
$$K_4FeCy_6 + ZnCO_3 = ZnK_2FeCy_6 + K_2CO_3.$$

Green gives the reaction between zinc nitrate and alkaline carbonate as follows, the zinc being supposed to form a basic carbonate:

$$2Zn(NO_3)_2 + 3K_2CO_3 + 2H_2O =$$
$$Zn(OH)_2ZnCO_3 + 2KHCO_3 + 4KNO_3,$$

and the corresponding reaction on addition of ferrocyanide:

$$Zn(OH)_2\ ZnCO_3 + K_4FeCy_6 =$$
$$Zn_2FeCy_6 + 2KOH + K_2CO_3,$$

a double ferrocyanide of doubtful composition being probably formed, so that the equation assumes the form:

$$Zn(OH)_2{\cdot}ZnCO_3 + xK_4FeCy_6 =$$
$$Zn_2FeCy_6{\cdot}(x - 1)\ K_4FeCy_6 + 2KOH + K_2CO_3.$$

See App., pp. 167, 168.

METHOD No. 3.

Estimation of Protective Alkali by Neutralizing with Potassium Bisulphate and Distilling.

A. F. Crosse (*Proceedings* Chem. and Met. Soc. South Africa) describes the following process: 500 c.c. of the solution are taken, 1 gram of potassium bisulphate ($KHSO_4$) added, and the liquid boiled in a retort with condenser for 45 minutes. The hydrocyanic acid distilled over is collected in caustic potash, and the resulting liquid titrated in the usual way with silver nitrate and potassium iodide. The reactions are as follows:

$$KHSO_4 + KCy = K_2SO_4 + HCy.$$

When alkali is present, a portion of the bisulphate is neutralized:

$$KHSO_4 + KOH = K_2SO_4 + H_2O,$$
$$KHSO_4 + K_2CO_3 = K_2SO_4 + KHCO_3,$$

and the amount of hydrocyanic acid given off is proportionately less.

From the first equation it is evident that in the absence of

protective alkali, 1 gram of $KHSO_4$ liberates 0.1985 gram of HCy.

The difference between the cyanide equivalent of the bisulphate used and the cyanide actually found in the distillate is the cyanide equivalent of the protective alkali, which may be converted into terms of KOH by multiplying by the factor $56/65 = 0.8615$.

An excess of free potassium cyanide must always be present, hence it is recommended to add 2 grams of chemically pure potassium cyanide before distilling. It is obvious, also, that the bisulphate must be added in excess of the amount required to neutralize the protective alkali.

While this method may possibly give accurate results with careful working, it is certainly very slow and cumbrous, and hardly adapted to the requirements of practical work. It is also probable that by boiling the cyanide solution for 45 minutes some decompositions would occur which would vitiate the result.

In the absence of sufficient free cyanide it is possible that a part of the bisulphate would be consumed in precipitating zinc cyanide,

$$K_2ZnCy_4 + 2KHSO_4 = ZnCy_2 + 2HCy + 2K_2SO_4,$$

but this would introduce no error, as an equivalent of HCy is liberated.

(C, D) Estimation of Hydrates, Carbonates and Bicarbonates.

The tests for these substances may conveniently be considered together, as most of the methods for estimating any one of them involves a determination of one of the others. The behavior of the various bodies individually towards different indicators, when neutralized by dilute acid, has already been described. It must be here remarked that hydrates and bicarbonates cannot coexist in the solution, as the reaction,

$$KOH + KHCO_3 = K_2CO_3 + H_2O,$$

or its equivalent, would immediately occur; hence we have to consider only the cases in which cyanides are present together with (*a*) hydrates and monocarbonates, (*b*) monocarbonates and bicarbonates.

(*a*) *Solution Contains Cyanides, Hydrates and Monocarbonates.* —From what has been said above (tests for total and protective alkali) it is clear that the equivalent of 'hydrate + ½ monocarbonate' may be found by titrating with standard acid and phenol phthaleïn

after addition of silver nitrate to produce turbidity; and the equivalent of 'cyanide + hydrate + monocarbonate' by direct titration of another portion of the solution with standard acid and methyl orange (without adding $AgNO_3$).

The cyanide may be found by any of the ordinary methods, and its alkali equivalent deducted from the last result, KCy × 0.8617 = KOH. We have then (A) = hydrate + ½ carbonate. (B) = hydrate + carbonate — whence hydrate = 2A—B, and carbonate = 2(B—A).

(*b*) *Solution Contains Cyanides, Carbonates and Bicarbonates.* —When no hydrate is present the titration with acid and phenol phthaleïn after addition of $AgNO_3$ gives us simply '½ carbonate,' while the direct titration with acid and methyl orange gives 'cyanide + carbonate + bicarbonate.'

Deducting cyanide as before, we have (A) = ½ carbonate (B) = carbonate + bicarbonate — whence carbonate = 2A, and bicarbonate = B—2A.

In presence of zinc double cyanide and ammonia further complications arise, and this method cannot be applied.

Method No. 2.

Estimation of Hydrates, Carbonates and Bicarbonates by Combined Titrations, with and without Addition of Barium Salts.

(A) Hydrates may be estimated by adding the necessary amount of a standard solution of barium chloride to precipitate the carbonate (avoiding an excess, which would tend to precipitate a portion of hydrate), filtering and titrating the filtrate, or a measured fraction of it, with standard acid and methyl orange. The result gives 'hydrate + cyanide,' from which the hydrate is obtained by deducting the equivalent of cyanide.

The reactions are:

$$BaCl_2 + K_2CO_3 = 2KCl + BaCO_3.$$

$$BaCl_2 + 2KHCO_3 = 2KCl + H_2O + CO_2 + BaCO_3.$$

(B) The precipitated barium carbonate, after thorough washing in boiling distilled water, is titrated with standard acid and methyl orange, which gives the equivalent of "carbonate + ½ bicarbonate."

(C) By adding an excess of alkaline hydrate free from CO_2

before addition of barium chloride, the whole of the carbonate and bicarbonate may be precipitated as $BaCO_3$:

$$KHCO_3 + KOH = H_2O + K_2CO_3,$$
$$BaCl_2 + K_2CO_3 = 2KCl + BaCO_3.$$

If the solution be now filtered and tested as before, the difference between the amount of hydrate added and the amount found after precipitation with barium chloride gives the equivalent of the bicarbonate, and titration of the washed precipitate gives the equivalent of 'carbonate + bicarbonate.' (For further details see Sutton, *Volum. Anal.*, 8th ed., pp. 60-63.) (See Appendix, p. 170.)

Modification in Presence of Zinc.—When zinc is present, Green modifies this process as follows (*Proceedings* Inst. Min. and Met., October, 1901): An excess of barium chloride is first added to the solution (sufficient to precipitate the sulphates and carbonates), then excess of potassium ferrocyanide, then twice the amount of silver nitrate necessary to indicate total cyanide, *viz.*, sufficient to precipitate the whole of the cyanide. A slight excess does not matter, as it merely precipitates some chloride, or, if no chlorides are present, some sulphocyanide or ferrocyanide. The zinc all occurs in the precipitate as ferrocyanide, and the alkaline hydrates are left in solution. (Barium chloride being present, the carbonates are already precipitated as $BaCO_3$.) Phenol phthaleïn is now added, and the solution titrated with N/10 nitric acid till colorless, or till it acquires the faint, greenish-yellow tinge produced by the excess of ferrocyanide.

Experiments which I have made with this process gave only moderately good results, the numbers being generally less than theoretical, perhaps owing to precipitation of some barium hydrate.

(E) Estimation of Ammonia.

Free ammonia and the carbonates and bicarbonates of ammonium are alkaline to methyl orange, and are estimated along with the other ingredients in titrating total alkali (see above). Ammonium chloride is neutral to all indicators.

Bettel (*Journal* Chem. and Met. Soc. South Africa, Vol. I., p. 168) gives the following method for estimating ammonia in cyanide solutions: "If sufficient nitrate of silver be added to a solution (say, 10 c.c.) to wholly precipitate the cyanogen compounds, and a drop or two of normal hydrochloric acid be then added, the whole made

up to 100 c.c. and shaken, then filtered, and 10 c.c. of the filtrate distilled with 150 c.c. water from a tubulated flask, and the steam condensed in a Liebig's condenser, the ammonia coming over may be readily estimated by color test with Nessler solution, and comparison with distilled water free from ammonia and standard ammonium chloride solution containing 0.01 gram NH_3 per liter, treated with Nessler solution."

If the ammonia in combination as ammonium salts is to be estimated, sodium carbonate must be added to the liquid to be distilled. (For further details as to distillation and colorimetric test, see Sutton, *Volum. Anal.*, 8th ed., pp. 447, 456.)

CLASS III.

REDUCING AGENTS.

General Remarks.—The efficiency of cyanide solutions for gold extraction depends, as already pointed out, not only on the amount of free cyanide present, but also on the amount of oxygen. Hence any substance which is capable of absorbing oxygen will exercise an injurious effect, and it is sometimes desirable to be able to determine the amount of such deoxidizing or reducing agent.

We shall first describe a general method for estimating the amount of reducing agent, irrespective of its actual composition, and afterwards discuss the methods in use for determining the amount of the various individual bodies commonly met with in cyanide solutions, which exercise a reducing influence.

This part of the subject will be considered under the following heads:

(*A*) Reducing Power.
(*B*) Ferrocyanides.
(*C*) Sulphocyanides (Thiocyanates).
(*D*) Sulphides.
(*E*) Other Reducing Agents, Such as Nitrites, Formates, etc.

SECTION A.

(1) Estimation of Reducing Power.

A rough idea of the relative quantities of reducing agent in various solutions may be obtained by comparing the amounts of standard permanganate required to give a permanent tint to equal volumes of the different solutions, tested under the same conditions, and acidified in each case with sulphuric acid.

Pure potassium cyanide and other simple cyanides, when treated in this way, give hardly any reaction with permanganate, a single drop of N/10 $KMnO_4$ added to the acidulated cyanide solution being generally sufficient to establish a permanent pink tint, owing

to the fact that the hydrocyanic acid liberated scarcely affects the permanganate at all. When ferrocyanides, sulphocyanides, sulphides, nitrites, formates, and some other substances are present, however, the pink color at first disappears rapidly as each drop is added. Towards the finish the disappearance is sometimes not sharp, the color fading when the solution is left standing for a few moments.

Indirect Estimation by Adding Excess of Permanganate.—When the finishing point is indefinite, it is perhaps better to determine the reducing power by adding to the acidulated solution a moderate excess of permanganate, allowing to stand for some time, then adding an excess of potassium iodide to the pink liquid until the color changes to brownish-yellow; in this reaction iodine is liberated in proportion to the excess of permanganate present. The iodine is then immediately determined by means of standard thiosulphate, using starch indicator. As the titration is performed in an acid liquid, a starch solution prepared with addition of caustic soda may conveniently be employed; this will keep for a long time, whereas the ordinary starch indicator must always be freshly prepared. Deducting the equivalent of the iodine thus found, in terms of standard permanganate, from the total amount of permanganate added, we have the quantity of permanganate which corresponds to the reducing agents present in the solution under examination.

In this process it is assumed that hydrocyanic acid has no action on iodine. The same assumption is made in the method for estimating cyanogen bromide, to be noticed below. It is possible, however, that some iodide of cyanogen (ICy) may be formed according to the reaction

$$HCy + I_2 = HI + ICy;$$

but this would introduce no error, as the cyanogen iodide is completely decomposed by the thiosulphate.

The permanganate may be standardized by adding excess of potassium iodide to a measured volume and determining the amount of thiosulphate required to destroy the color.

The starch indicator should be added near the finish, after sufficient standard thiosulphate has been run in to nearly discharge the original yellow color of the iodine.*

* Instead of using potassium iodide and thiosulphate, the excess of permanganate might be determined by means of standard oxalic acid. When the amount of reducing agent is small, N/100 solutions of permanganate, etc., should be used.

The standard solutions which may be conveniently used are: (1) Potassium permanganate, $KMnO_4$, 3.1606 grams per liter (decinormal solution). (2) Sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$, 24.822 grams per liter (decinormal solution). (3) Potassium iodide, KI, 16.602 grams per liter. (The solid salt may be used instead of the latter solution.)

The probable reactions are:

$$(a)\ 5KI + KMnO_4 + 4H_2SO_4 = MnSO_4 + 3K_2SO_4 + 4H_2O + 5I.$$

$$(b)\ 2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

Definition of Reducing Power.—For the sake of precision in comparative tests we may define the 'reducing power' of a solution as the number of cubic centimeters of N/10 permanganate (3.16 grams per liter) which must be added to give a permanent coloration with 1 c.c. of the solution to be examined, a sufficient amount of free sulphuric acid being present in every case.

(2) Estimation of Oxidizable Organic Matter.

Bettel (*Proceedings* Chem. and Met. Soc. South Africa, Vol. I., p. 166) gives a method somewhat similar to that just described, as follows: "In treating spruit tailings, or material containing decaying vegetable matter, I offer the following method for testing colored solutions:

"(*a*) Prepare a solution of a sulphocyanide so that 1 c.c. sulphocyanide = 1 c.c. N/100 $KMnO_4$.

"(*b*) To 50 c.c. of the liquid to be tested add sulphuric acid in excess, and then a large excess of N/100 permanganate. Keep at 60°-70° for an hour, then cool and titrate back with the sulphocyanide solution.

"Result:

O_2 consumed in oxidizing organic matter +
O_2 consumed in oxidizing K_4FeCy_6 +
O_2 consumed in oxidizing KCNS.

"After estimating KCNS and K_4FeCy_6, a simple calculation gives the oxygen to oxidize organic matter. The result, multiplied by 9 will give, approximately, the amount of organic matter present."

In order to prepare another portion of the solution for the estimation of ferrocyanides and sulphocyanides, he proceeds as follows: The solution is shaken up with powdered quicklime and filtered,

it is then "of a faint straw color, and is in a proper condition for analysis. In such clarified solution the oxidizable organic matter is no longer present and the ferro and sulphocyanogen estimations are readily performed."

SECTION B.

Estimation of Ferrocyanides.

A very large number of methods have been used or proposed for the estimation of ferrocyanides, both in cyanide solutions and in various commercial products in which they occur mixed with other bodies. These processes may be classified as follows:

(*A*) Those depending on the conversion of ferrocyanide into ferricyanide in presence of free acid by the action of $KMnO_4$.

(*B*) Those depending on the precipitation of ferrocyanide as Prussian blue by means of ferric salts.

(*C*) Those depending on the reactions of ferro- or ferricyanides with copper salts.

(*D*) Those depending on the reactions of ferrocyanides with zinc salts.

(*E*) Those depending on the estimation of the iron after complete decomposition of the ferrocyanogen by means of strong acids.

Group (A).—Estimation of Ferrocyanides by Conversion into Ferricyanides in Acid Solution by Means of Permanganate.

Method No. 1.

Direct Titration of the Solution.

This process, due to de Haen, is described in Fresenius (*Quant. Anal.*, 7th ed., Vol. I., p. 378) and Sutton (*Volum. Anal.*, 8th ed., p. 226).

In all cases where the solution contains no other reducing agent the amount of ferrocyanide may be estimated with tolerable accuracy by this method, since, as pointed out above, the presence of

cyanides, which are converted on acidulating into hydrocyanic acid, does not interfere. When much ferrocyanide is present the solution must be considerably diluted with water, otherwise the end-point is not sharp. About 100 c.c. of water should be added for every 0.1 gram of ferrocyanide present.

A N/10 solution of ferrocyanide contains 42.2358 grams $K_4FeCy_6 \cdot 3H_2O$ per liter, corresponding volume for volume with N/10 permanganate containing 3.1606 grams $KMnO_4$ per liter. In practice N/20 or N/100 solutions may be more conveniently used.

The finishing point is shown by the change from yellow to reddish-yellow. Ferric chloride may also be used as an external indicator; the reaction is considered to be complete when a drop of the liquid on a white plate no longer gives a blue tinge with a drop of ferric chloride.

The reaction of permanganate on ferrocyanide in presence of sulphuric acid may be represented as follows:

$$KMnO_4 + 5K_4FeCy_6 + 4H_2SO_4 = 3K_2SO_4 + MnSO_4 + 4H_2O + 5K_3FeCy_6.$$

Method No. 2.

Precipitation of Ferrocyanide as Prussian Blue, and Subsequent Solution in Alkalis and Titration with Permanganate.

This modification of de Haen's method was introduced by Erlenmeyer for the purpose of separating sulphocyanides, and other reducing agents from the ferrocyanide, before titration with permanganate (Emil Erlenmeyer, Wagner's *Jahresbericht,* 1860, p. 223). Thorpe (*Dict. of Applied Chemistry,* Art. 'Cyanide,' p. 631) states that of the many methods proposed, Erlenmeyer's is probably the most exact.

The ferrocyanogen is precipitated by an excess of ferric chloride in the presence of an excess of hydrochloric acid, as Prussian blue, which he filters off, washes and decomposes by means of caustic potash.

(*a*) $3K_4FeCy_6 + 2Fe_2Cl_6 = Fe_4(FeCy_6)_3 + 12KCl.$

(*b*) $Fe_4(FeCy_6)_3 + 12KOH = 3K_4FeCy_6 + 2Fe_2(OH)_6.$

The ferric hydrate is then filtered off, and the ferrocyanogen determined in the acidified filtrate by titration with $KMnO_4$ according to de Haen's method.

With regard to this process Bettel remarks (*Proceedings* Chem.

and Met. Soc. South Africa, Vol. I., p. 220), "the decomposition of the Prussian blue by alkali and subsequent titration of the ferrocyanide formed is inaccurate on account of the incomplete decomposition of the ferric ferrocyanide by potash." Bettel suggests the following method.

Method No. 3.

Estimation of Ferrocyanide by Addition of the Solution to be Tested to a Known Amount of Acid Permanganate.*

In the absence of organic matter, an acidified solution of a simple cyanide such as KCy or of a double cyanide (as K_2ZnCy_4), *i.e.*, a solution of HCy, is not affected by dilute permanganate.

In presence of zinc, the method is as follows:

(*a*) A burette is filled with the cyanide solution to be tested, and the liquid run into 10 or 20 c.c. of N/100 permanganate, strongly acidified with H_2SO_4 until the color is just discharged. Result = A (calculated for 50 c.c. of original solution).

(*b*) A solution of ferric sulphate or chloride is acidified with sulphuric acid and 50 c.c. of the cyanide solution poured in. After shaking for about half a minute, the Prussian blue is separated from the liquid by filtration and the precipitate and filter paper washed. The filtrate is next titrated with N/100 $KMnO_4$. Result = B. Equivalent of ferrocyanide = A—B.

In this process the first titration estimates all the reducing agents, and the second, all except ferrocyanides, hence the difference of the two gives the ferrocyanide.

Method No. 4.

Estimation of Ferrocyanide by Preliminary Oxidation to Ferricyanide, then Boiling with Alkali and Ferrous Salt to Convert Again into Ferrocyanide, Finally Titrating with Permanganate.

J. Tcherniac (*Chemical News,* Vol. XLVII., p. 254, abstract from paper in *Zeitschrift f. analyt. Chem.* 1883) gives the following method:

The solutions required are: (*a*) A saturated solution of potassium permanganate; (*b*) A standard permanganate solution of which

* *Proceedings* Chem. and Met. Soc. South Africa.

1 c.c. corresponds to 0.1 gram K_4FeCy_6; (*c*) A solution of ferrous sulphate containing 50 to 100 grams per liter.

The method as originally described is as follows:

A measured quantity of the solution to be tested, containing about 3 grams ferrocyanide, is made up to 500 c.c. with sulphuric acid in a thin measuring flask, and mixed with so much of the saturated permanganate that the red color does not disappear on agitation for some minutes. The whole is allowed to stand for about half an hour (for complete oxidation of ferrocyanides, thiocyanates, sulphides, etc.); after the oxidation is complete, caustic soda is added in large excess, and the whole is heated to a boil, with constant stirring. The hot solution is mixed with so much ferrous sulphate that the precipitate is colored black by the ferroso-ferric oxide liberated, allowed to cool, filled up to the mark again, and filtered. In an aliquot part of the filtrate (say, 250 c.c.) the quantity of ferrocyanogen re-formed by the ferrous sulphate is determined by titration with the standard permanganate after acidulation with sulphuric acid.

This method is described by Alfred Adair (*Journal* Chem. and Met. Soc. South Africa, Vol. III., p. 140) with a slight modification, by which it may be applied for the estimation of cyanogen in commercial cyanide. He states that in the treatment with saturated permanganate the ferrocyanide is oxidized to ferricyanide only, whereas cyanates, sulphocyanides and other impurities are either destructively oxidized, or converted into substances which do not interfere with the final reduction of ferri- to ferrocyanide, and the titration of the latter with permanganate. He also states that estimations can be made in 15 minutes, and that concordant results are obtained by different operators.

Adair's modification of Tcherniac's method is as follows:

The solutions required are: (*a*) 25 per cent caustic alkali; (*b*) 20 per cent H_2SO_4, pure; (*c*) saturated solution of $KMnO_4$; (*d*) saturated solution of $FeSO_4$; (*e*) N/10 $KMnO_4$, or, more conveniently, a solution such that 1 c.c. = 0.100 gram total cyanogen.

The permanganate solution (*e*) is standardized as follows: Three grams of potassium ferrocyanide, $K_4FeCy_6 \cdot 3H_2O$, are dissolved in 300 c.c. water, and 15 c.c. of the 20 per cent H_2SO_4 (*b*) are added, then if n equals number of c.c. of solution (*e*) consumed

$$\frac{880 \times 3}{157.9\, n} = \text{Value of Cy in grams per c.c.}$$

(*i*) Ten grams of the commercial cyanide are weighed into a liter flask, and about 200 c.c. water added to dissolve it. Add 2 c.c. of the alkali solution (*a*) and a quantity of the ferrous sulphate solution (*d*) equal to 12 grams $FeSO_4 \cdot 7H_2O$. Add the latter 5 c.c. at a time, and shake well.

$$6KCy + FeSO_4 + \text{alkali} = K_4FeCy_6 + K_2SO_4 + \text{alkali}.$$

The reaction is immediate.

[This step, of course, would be omitted where the method is applied for estimating ferrocyanides only.]

(*ii*) Add sulphuric acid until Prussian blue is formed, then 15 c.c. of the sulphuric acid solution (*b*) and saturated solution of permanganate (*c*), until the color remains persistent; the color can be seen through the edges. An excess of 1 or 2 c.c. or more does not matter. The above quantity of acid is enough for each gram of $KMnO_4$ added, but if more than 1 gram of $KMnO_4$ is used, acid must be added in the same proportion, *viz.:* 15 c.c. to each gram of $KMnO_4$ used. If much sulphocyanide is present, allow to stand 15 minutes, and, if necessary, a further addition of $KMnO_4$ may be made. The reaction is given above (under Method No. 1).

(*iii*) Next add ferrous sulphate solution (*d*) in quantity equal to 15 grams, and immediately 15 c.c. alkali solution (*a*). The liquid must be strongly alkaline. Shake thoroughly and make up to the mark, again mixing thoroughly. The reaction is:

$$K_3FeCy_6 + FeSO_4 + 3KOH =$$
$$K_4FeCy_6 + Fe(OH)_3 + K_2SO_4.$$

[This is the simplest possibility, but it may be $2K_3FeCy_6 + 3FeSO_4 = Fe_3(FeCy_6)_2 + 3K_2SO_4$ and $Fe_3(FeCy_6)_2 + 8KOH = 2K_4FeCy_6 + Fe_3O_4 \cdot 4H_2O$.]

(*iv*) Filter through a large folded filter. The titration is completed by taking 500 c.c., or an aliquot portion, adding 20 c.c. H_2SO_4, and then running in the required amount of the standard $KMnO_4$ (*e*).

The influence of the precipitate on the results is small. It may be ascertained by testing a weighed portion of pure $K_4FeCy_6 + 3H_2O$, adding the quantities of solutions, as for an impure sample.

Thorpe (*Dict. of Applied Chemistry,* Art. 'Cyanide,' p. 633) criticises Tcherniac's method as applied to the determination of actual ferrocyanide in the crude product obtained in the process of manufacture. After giving an outline of the process he says:

"Tcherniac does not direct us to maintain a red color in the mixture by occasional addition of more permanganate, but he no doubt means us to do so. At last the mixture is made strongly alkaline by addition of caustic soda, heated to boiling and mixed with ferrous sulphate to reconvert the red into yellow prussiate with formation of magnetic oxide of iron, which is filtered off. The filtrate is acidified, and its prussiate (*i.e.*, ferrocyanide) determined by titration with a standard solution of permanganate (de Haen's method). The method obviously is based on the presumption that in the first process of oxidation the thiocyanate is converted into substances not susceptible of conversion into prussiate by treatment with ferrous hydrate and caustic alkali; but this we believe is a mistake; as shown by Erlenmeyer, permanganate in acid solution converts thiocyanate into cyanide and sulphate, and the HCy, as far as it survives, will be reported as so much prussiate."

$$6KCy + Fe(OH)_2 = K_4FeCy_6 + 2KOH.$$

Method No. 5.

Precipitation of Ferrocyanide with Alcohol and Subsequent Titration with Permanganate.

J. Tcherniac (*Zeitschrift f. Anal. Chem.*, abstracted in *Chemical News*, Vol. XLVII., p. 254), operates as follows:

"Ten c.c. of the solution is poured into 70 c.c. of alcohol of 95 per cent, to which a little acetic acid has been previously added. The precipitated ferrocyanide, after washing with alcohol of 90 per cent until the washings are colorless, is dried at 100° C. on the filter, dissolved in water, and titrated with permanganate solution." The method would probably be applicable only to very concentrated solutions.

Group (B).—Estimation of Ferrocyanides by Precipitation as Prussian Blue.

Fresenius (*Quant. Anal.*, 7th ed., Vol. I., p. 380) gives the following method, due to H. Rheineck (*Chem. Centralbl.*, 1871, p. 778), which may possibly be of use in certain cases: It depends on the fact that when a solution of a ferric salt (sulphate or chloride) is added with vigorous agitation to a liquid containing ferrocyanide,

no matter whether a mineral acid is present or not, at first a clear blue fluid is produced, which becomes afterwards turbid, and when all the ferrocyanogen is exactly thrown down a flocculent precipitate of Prussian blue appears suspended in a clear colorless fluid. A certain measure of the liquid under examination is taken, and the same measure of a standard solution of ferrocyanide of potassium; to these are added a solution of ferric chloride from a burette till the flocculent precipitate separates.

In the case of alkaline liquids the solution must be first acidulated with dilute H_2SO_4 or HNO_3. If thiocyanates be present, the least excess of iron solution will cause the liquid to assume a deep red color. The change from blue to red furnishes a very definite end-reaction.

Group (C).—Estimation of Ferrocyanides by Reactions with Copper Salts.

Method No. 1.

Estimation by Titration with Copper Sulphate Using Ferric Chloride as Indicated.

Fresenius (*Quant. Anal.*, 7th ed., Vol. I., p. 380) describes the following method, due to E. Bohlig (*Polytechn. Notizblatt*, pp. 16, 81),* as accurate enough for technical purposes. The standard solutions required are 1 per cent copper sulphate, $CuSO_4 \cdot 5H_2O$ and 0.4 per cent potassium ferrocyanide, $K_4FeCy_6 \cdot 3H_2O$. The solution to be tested is titrated with the standard copper solution after acidifying with dilute sulphuric acid, until a strip of filter paper dipped into the mixture no longer becomes blue when a drop of ferric chloride is put on it.

Any sulphide present in the liquid must first be removed by boiling with lead carbonate and filtering.

The method depends on the precipitation of the brownish-red ferrocyanide of copper.

$$2CuSO_4 + K_4FeCy_6 = 2K_2SO_4 + Cu_2FeCy_6.$$

For standardizing the copper solution about 0.2 gram of ferrocyanide dissolved in 50 c.c. of water may be used.

My experiments with this method show that while cyanides and

* See also Wagner, Jahresbericht, 1861, p. 237.

thiocyanates do not appreciably interfere, the presence of zinc double cyanide renders the method useless, as a part (and in some cases the whole) of the ferrocyanogen is precipitated as ferrocyanide of zinc, and is not determined in the titration.

Method No. 2.

Titration with Copper Sulphate after Adding Ferric Chloride, Filtering off Prussian Blue and Treating with Alkali.

O. Knublauch (*Journal* Soc. Chem. Ind., Vol. VIII., p. 732, 1889) gives a method originally intended for the estimation of ferrocyanogen in spent material from gas purification, but which may be adapted for the analysis of cyanide solutions. He finds that the previous method (direct titration with copper sulphate) is affected by impurities which either react with the copper or impair the delicacy of the end-reaction.

The method proposed is as follows: A measured volume of the liquid to be tested, say, 100 c.c., is run into a sufficient excess of hot ferric chloride containing hydrochloric acid. (The solution recommended contains, per liter, 60 grams ferric chloride and 200 c.c. of hydrochloric acid sp. gr. 1.19.) The mixture is then filtered at 80° C. through a folded filter, covered over, in a hot-water funnel, and the precipitate washed rapidly with hot water. The filter paper with the precipitate is then spread in a porcelain dish and treated with 20 c.c. of 10 per cent caustic potash, taking care that none of the Prussian blue escapes decomposition. The liquid is then filtered, and if free from sulphides it may be titrated at once, after acidifying with sulphuric acid. In each test 2.5 to 5 c.c. of sulphuric acid (1 : 5) are used.

If sulphides are present, the liquid must first be treated with 1 or 2 grams of lead carbonate and filtered.

The copper sulphate solution used contains 12 to 13 grams per liter, and is standardized by titrating with a pure ferrocyanide solution containing 4 grams per liter.

The finishing point may be found either by 'spot test' or 'filter test.'

In the spot test, a little of the liquid is taken out on a glass rod and placed on a filter paper. Ordinary white filter paper generally contains sufficient iron to give a blue color so long as ferrocyanide is

in excess, or a drop of very dilute ferric chloride may be placed on the paper near the spot, so that the reaction is observed at the contact of the two liquids. When the blue color ceases to be formed, the titration is complete.

In the filter test a portion of the liquid is carefully filtered through a minute filter, and the clear liquid tested with ferric chloride; this is the more delicate test and always registers slightly higher than the spot test.

Care must be taken to always use the same proportion of acid in the titration, and to allow in all cases the same time for the copper sulphate to react, and for the blue color to appear in testing (2 minutes in the spot test and one-quarter to one-half minute in the filter test). As a rule the spot and filter titrations only differ from 0.2 to 0.6 c.c. of copper solution, when from 8 to 12 c.c. of the above standard have been used, and the finishing point may be determined to 0.2 c.c.

Special Modification of Knublauch's Method.—In some cases, instead of the blue color disappearing sharply at a certain stage, it is found that the solution, in the filter test, remains persistently green or greenish-yellow, so that the filter test registers much higher than the spot test; moreover, in such cases the spot test with ferric chloride registers higher than the spot test on filter paper alone. This is stated to be due to the presence of other substances containing iron and cyanogen in varying quantities, and also containing sulphur. These substances appear to undergo gradual decomposition, yielding ferrocyanides, and they are also decomposed by potash and precipitated by ferric chloride.

The modified method proposed in such cases is as follows: Add to 200 or 300 c.c. of the solution, slightly more copper sulphate solution than is required by the spot titration; filter, pour the filtrate into hot ferric chloride (to precipitate any residual ferrocyanogen not indicated by the copper titration); decompose and titrate the Prussian blue formed, and, if it is thought desirable, the filtrate from this precipitate is treated in the same manner. The numbers obtained in this way are added as corrections to the numbers obtained in the usual manner, and it is then found that the spot and filter titrations approximate more and more, the latter becoming less, the former increasing. It therefore seems that in these cases the spot test shows too little and the filter test too much.

Method No. 3.

Estimation of Ferrocyanides by Conversion into Ferricyanides, and Titration with Copper Nitrate with Ferrous Sulphate as External Indicator.

F. Hurter (*Chemical News,* Vol. XXXIX., p. 25) describes the following method for determining small quantities of ferrocyanides in presence of cyanates, thiocyanates, cyanides, sulphides and thiosulphates: 100 c.c. of the solution are boiled with solution of bleaching powder, in quantity sufficient to convert all sulphides and thiosulphates into sulphates, and the ferrocyanide into ferricyanide. The liquid is then acidified and freed, as far as possible, from the excess of chlorine by warming and agitating it. It is then titrated with N/20 solution of cupric nitrate, prepared by dissolving 3.1785 grams of metallic copper in as little nitric acid as possible, and diluting to one liter. On adding this solution to the acidulated liquid containing ferricyanide, a yellow precipitate of cupric ferricyanide is formed.* Drops of the thoroughly mixed liquid are taken up with a glass rod and added to drops of a 1 per cent solution of crystallized ferrous sulphate on a porcelain plate. As long as insufficient copper solution has been added to combine with the whole of the ferricyanide present, the deep blue ferrous ferricyanide is formed on the porcelain. When the liquid no longer contains soluble ferricyanide the indicator acts on the copper precipitate, and reduces it to the characteristic chocolate-colored cupric ferrocyanide. Hence the end of the reaction is indicated by a brown color being produced on the porcelain instead of the blue first obtained. Each c.c. of the copper solution added before this result is obtained represents 0.01013 gram of Na_4FeCy_6 in the liquid. The method is not suitable for the determination of large quantities of ferrocyanides, as the color of the copper precipitate obscures the blue color, and the precipitate is not always of definite composition.

It is evident that this process is also adapted for the direct estimation of small quantities of ferricyanide.

A practically identical method is described by Sutton (*Volum. Anal.,* 8th ed., p. 226).

Method No. 3 (*a*).—The following modification of Hurter's

* $Cu_3(FeCy_6)_2$.

method appears to be a simple and accurate method of estimating ferrocyanides in presence of zinc.

1. Heat the solution to about 80° C., make strongly alkaline with NaOH, add Na_2S in slight excess, agitate, settle, filter and wash well with hot water. The filtrate is practically free from zinc.

2. Cool the solution, acidulate with H_2SO_4, and add N/10 $KMnO_4$ till H_2S and other reducing agents are completely oxidized, and a faint reddish tint is permanent.

3. Titrate with standard copper sulphate solution, using ferrous ammonium sulphate as indicator, in spots, on a white plate. The end point is very sharp and definite.

Group (D).—Estimation of Ferrocyanide by Reactions with Zinc Salts.

Method No. 1.

Titration with Zinc Sulphate, Using Ferric Chloride as Indicator.

A method based on this principle is described by J. Müller (Wagner's *Jahresbericht,* 1861, p. 238), and K. Zulkowski (*Jahresbericht,* 1883, p. 491). According to the latter, constant results can only be obtained with hot solutions. A suitable standard is obtained by dissolving 111 grams of the double salt ($ZnSO_4 \cdot K_2SO_4 \cdot 6H_2O$) in water and diluting to one liter.

Ten c.c. of this zinc solution are measured out, mixed with 5 c.c. of dilute sulphuric acid (1 : 5) and 20 c.c. of water, and the whole is heated to boiling. The solution to be tested is run from a burette into the hot liquid until, when a drop of the mixture is put on a piece of filter paper and a drop of very dilute ferric chloride solution put on the zone of paper soaked in the solution, it just produces a blue color. The precipitate remains localized in the place where the drop was put down. The zinc solution should be standardized on a model solution prepared from pure ferrocyanide, containing approximately the same percentage as the solution to be tested. According to Thorpe (*Dict. of Applied Chemistry,* Art. 'Cyanide') the method gives only moderately exact results.

In applying the above process R. Gasch (Abstract in *Journal* Chem. Soc., 1890, p. 834) employs a 1 per cent solution of uranium acetate, instead of ferric chloride. With this indicator, ferrocyanides

give a brown coloration. Gasch also uses a standard 2 per cent solution of potassium ferrocyanide, against which he titrates the zinc solution, instead of using a standard solution of zinc sulphate, as in Zulkowsky's original process.

When the ferrocyanide is only present in very small amount it is preferably precipitated as Prussian blue, filtered and dissolved in caustic alkali solution, after which it is titrated as described above.

Method No. 2.

Estimation of Ferrocyanide by Titration of Alkali Generated on Addition of Zinc Carbonate.

The following method is described by R. Zaloziecki (*Zeitschrift f. Anal. Chem.*, Vol. XXX., p. 484; see abstract in *Chemical News*, 1891, p. 207). It is based on the fact that ferrocyanide of potassium or sodium may be completely precipitated, in the form of double ferrocyanide of zinc and alkali metal, by the addition of zinc carbonate, and subsequent passage of a current of carbonic acid gas. The double ferrocyanide is then transformed into the corresponding sodium or potassium carbonate, and the quantity of ferrocyanide originally present found by titrating the alkaline carbonate formed. According to Zaloziecki, 3 molecules of K_4FeCy_6 yield on decomposition 2 molecules of Zn_2FeCy_6, whilst 1 molecule of K_4FeCy_6 remains undecomposed. The double salt, therefore, corresponds to the formula,

$$2Zn_2FeCy_6 + K_4FeCy_6,$$

its decomposition by zinc carbonate being represented by the following equation:

$$3K_4FeCy_6 + 4ZnCO_3 = (2Zn_2FeCy_6)\cdot K_4FeCy_6 + 4K_2CO_3.$$

With potassium ferrocyanide the reaction takes place hot or cold. With sodium ferrocyanide the above reaction only takes place in hot solutions, the reaction in the cold giving a double salt poorer in zinc. For this reason it is necessary always to operate with hot solutions. Four parts of carbonate found should correspond to three parts of ferrocyanide in the original substances.

When cyanides or other substances alkaline to the indicator used are also present, they must, of course, be removed or allowed for. This reaction between ferrocyanides and zinc carbonate forms the basis of the methods recently described (Oct., 1901) by L. M.

Green, in a paper laid before the Institute of Mining and Metallurgy for estimating zinc, ferrocyanides and alkali in cyanide solutions containing zinc. The method will be more conveniently discussed in connection with the determination of zinc.

Group (E).—Estimation of Ferrocyanide by Determining the Iron Contents after Complete Decomposition of Ferrocyanogen.

Method No. 1.

Treatment by Evaporation with Mineral Acids.

According to W. J. Sharwood (*Engineering and Mining Journal,* 1898, p. 216), the methods for estimation of ferrocyanides and thiocyanates based upon oxidation by permanganate were found to be totally unreliable when tested experimentally upon solutions containing known quantities of the substances accompanying them in cyanide solutions.

He therefore takes 100 c.c. of the solution, evaporates twice with nitric acid, redissolves the residue in dilute sulphuric acid, and precipitates the iron by excess of ammonia. The precipitate is then at once redissolved in hydrochloric acid, and the iron estimated colorimetrically as thiocyanate, unless the quantity is sufficient to allow of reduction by zinc and titration with permanganate,

$$Fe \times 7.562 = K_4FeCy_6 \cdot 3H_2O.$$

The method advocated by Moldenhauer and Leybold (see Allen, *Comm. Org. Anal.,* Vol. III., pt. 3, p. 467) is practically identical with the above.

Method No. 2.

Decomposition of Ferrocyanide after Precipitation as Prussian Blue.

The following method, due to W. Leybold (*Journ. f. Gasbeleuchtung,* XXXIII., pp. 427-428),* is intended specially for the estimation of cyanogen in coal gas, this impurity being removed and converted into ferrocyanide by passing the gas through vessels containing

* See also *Journal* Soc. Chem. Ind., Vol. IX., pp. 923-979, 1890.

ferrous hydrate. The method, so far as concerns the estimation of ferrocyanide, is as follows:

The filtered liquid is acidified with HCl and ferric chloride (1:10) added in excess. The precipitate of Prussian blue is filtered off and washed till the washings are colorless, put in a beaker with the filter paper and a little caustic soda added. After decomposition, the ferric oxide is filtered off and washed till free from ferrocyanogen. The filtrate is then evaporated in a platinum basin to about 30 c.c. and strongly acidified with sulphuric acid (1:10), evaporated to dryness and ignited. The residue is then extracted with 100 c.c. of dilute sulphuric acid, washed with 50 c.c. of water and poured into a 250 c.c. flask. One c.c. of copper sulphate solution (1:10) and 10 grams of pure zinc are added, and the whole allowed to stand till completely reduced. The iron is then determined by permanganate in the usual way. (See App., p. 172.)

Comparative Tests with Different Methods of Estimating Ferrocyanide.

A model solution was prepared of the following theoretical composition:

Free cyanide, 0.2%. Thiocyanate, KCyS, 0.04%.
Cyanide as K_2ZnCy_4, 0.2%. Sodium bicarbonate, 0.39%.
Ferrocyanide, $K_4FeCy_6 \cdot 3H_2O$, 0.2%. Sodium carbonate, 0.06%.
Ammonium chloride, 0.1%.

This was tested for ferrocyanide:

(A) By evaporation with acids and determination of total iron (Group E, No. 1).

(B) By Erlenmeyer's method (Group A, No. 2).

The results were:

Method A.	Method B.
0.203%	0.203%
0.211%	0.219%
0.207%	0.194%
Mean, 0.207%	0.205%

Tests made by Bettel's method (running liquid to be tested into acidulated permanganate) were indefinite and totally erroneous. For further tests, see pp. 143–160.

SECTION C.

Estimation of Thiocyanates (Sulphocyanides).

The methods proposed may be classified as follows:

(A) Methods depending on oxidation of thiocyanate by permanganate.

(B) Methods depending on oxidation of thiocyanate by iodine in neutral solution.

(C) Colorimetric method, using ferric salts.

(D) Precipitation with copper salts in presence of a reducing agent.

Group (A).—Estimation of Thiocyanates by Oxidation with Permanganate.

This method has been already alluded to in discussing the reactions of permanganate with ferrocyanides, and in connection with Bettel's method (see p. 75) for estimating the latter. It depends on the reaction:

$$6KMnO_4 + 12H_2SO_4 + 5KCyS =$$
$$11KHSO_4 + 6MnSO_4 + 5HCy + 4H_2O.$$

It will be observed that the reducing power of thiocyanates is much greater, weight for weight, than that of ferrocyanides, since

1 c.c. N/100 $KMnO_4$ = 0.00016193 gram KCyS,
= 0.0036831 gram K_4FeCy_6.

Hence it is preferable to use a N/10 solution of permanganate in this case.

When ferrocyanides are also present they may be separated by precipitation as Prussian blue as already described, but the precipitate must be very thoroughly washed. Other forms of oxidizable organic matter are previously removed by shaking with lime and filtering. (See above.)

Group (B).—Estimation of Thiocyanates by Oxidation with Iodine.*

Thiocyanates (sulphocyanides) react with iodine in presence of an alkaline bicarbonate, as follows:

* Rupp and Schied: *Berichte* 35 [12], 2191-2195; see also *Journal* Soc. Chem. Ind., 1902, Oct. 31.

$$KCNS + KHCO_3 + 8I + 3H_2O = KHSO_4 + 6HI + CO_2 + KI + ICN.$$

In the first account of the method, the following description is given: "A known quantity of thiocyanate solution is allowed to stand with excess of N/10 iodine and about 1 gram of sodium bicarbonate in a stoppered bottle for half an hour in the dark, and the excess of iodine titrated with sodium thiosulphate."

A. Thiel (*Berichte,* 35 [15], 2766), gives a modification of this as follows: "Ten c.c. of the thiocyanate solution and 2 grams of sodium bicarbonate, with sufficient water to effect complete solution, are placed in a loosely-stoppered flask with 50 c.c. of N/5 iodine solution, and allowed to stand at room temperature for four hours. N/2 hydrochloric acid is then added, and the excess of iodine titrated with N/10 thiosulphate solution."

Rupp and Schied state that the presence of cyanogen iodide prevents the use of starch as an indicator, and on account of the yellow color produced by the same compound with KI, it is advisable to work with such quantities that not more than 20 c.c. of iodine solution are required. The end of the reaction is shown by the disappearance of the yellow color. Shaking the bottle should be avoided in order to prevent the evolution of carbonic acid. The method gives good results in presence of chlorides.

Procedure in Presence of Cyanides.—In presence of cyanides, boiling with about ½ gram of tartaric acid for 15 minutes in an open flask is sufficient to get rid of all hydrocyanic acid and the thiocyanate may then be estimated as above. In the same way a mixture of thiocyanate with chloride and cyanide may be estimated thus: (*a*) 10 c.c. of the solution are precipitated with 20 c.c. of $AgNO_3$, acidulated with HNO_3, the solution made up to 100 c.c. and filtered, the excess of silver being estimated in the filtrate with N/10 KCNS. (Volhard's method.) Result (*a*). Fifty c.c. of the original solution are boiled for 15 minutes with 1 gram of tartaric acid to decompose the cyanide, and the solution made up to 100 c.c. In 20 c.c. of this diluted solution the chloride and thiocyanate are determined by Volhard's method. Result (*b*). And in a further 10 c.c. the thiocyanate (alone) is estimated with iodine as above. Result (*c*).

$$(a) = KCl + KCNS + KCN.$$
$$(b) = KCl + KCNS.$$
$$(c) = KCNS.$$

I may add that I have tested this method, with satisfactory results. When zinc is present, a precipitate occurs on boiling with tartaric acid, but this may be filtered off and the thiocyanate estimated in the filtrate without difficulty.

Group (C).—Estimation of Thiocyanates by Colorimetric Method.

As is well known, ferric salts give a very delicate reaction for thiocyanates; a very small trace is sufficient to produce in neutral or slightly acid solutions an intense and characteristic blood-red tinge.

The test may be made as follows (W. J. Sharwood, *Engineering and Mining Journal,* 1898, p. 216): 10 or 20 c.c. of the solution to be tested are acidulated with hydrochloric acid, ferric chloride added, and the color compared with that produced by standard thiocyanate under the same conditions. When ferrocyanides are also present the precipitate formed must be filtered off before the tint can be compared, and the precipitate well washed.

See Appendix, page 174.

Group (D).—Estimation of Thiocyanates by Precipitation as Cuprous Salt, Using Ferrocyanide as Indicator.*

This method depends upon the fact that when a solution of a cupric salt is added to a solution of a thiocyanate in presence of a reducing agent, such as sodium bisulphite, the insoluble cuprous salt of thiocyanic acid is precipitated, the end of the reaction being ascertained by a drop of the solution in the flask giving a brown coloration when brought in contact with a drop of ferrocyanide.

The following reaction takes place:

$$2CuSO_4 + 2KCNS + Na_2S_2O_3 + H_2O = Cu_2S(SCN)_2 + K_2SO_4 + 2NaHSO_4.$$

The solutions required are:

(1) A standard solution of cupric sulphate, $CuSO_4 \cdot 5H_2O$, containing 6.243 grams per liter, 1 c.c. of which is equivalent to 0.001452 gram SCN.

(2) A solution of sodium bisulphite of sp. gr. 1.3.

(3) A solution of potassium ferrocyanide 1:20.

The liquid to be tested must be boiled after addition of the bisulphite, about 3 c.c. of the latter to 25 c.c. of the liquid to be examined. A measured volume of the copper solution is then run in,

* Barnes and Liddle, *Journal* Soc. Chem. Ind. II., p. 122; see also Sutton, *Volum. Anal.*, 8th ed., p. 228.

well shaken, and the precipitate allowed to settle for about a minute. A drop taken out on a glass rod and brought in contact with a drop of ferrocyanide on a white plate gives an immediate brown coloration as soon as an excess of copper is present. The change must be immediate, as a brown color develops on standing, even when the reaction is not complete. The test should be repeated after a preliminary approximation has been obtained, finally adding the copper solution drop by drop when near the finishing point.

See Appendix, pages 173, 175.

SECTION D.

Estimation of Sulphides.

Alkaline sulphides are rarely found in working cyanide solutions, although a small percentage frequently occurs in samples of commercial cyanide. Where the zinc precipitation process is used, it is probable that the zinc double cyanide in the solution precipitates as ZnS any small quantity of sulphide which may be present.

When soluble sulphides occur in the solution or in commercial cyanide, they may be estimated by one or other of the following methods:

1. Gravimetrically, in several ways; for example, by precipitation with lead salts, and subsequent oxidation to sulphate.
2. By precipitation as lead sulphide, and conversion into sulphocyanide by means of pure cyanide.
3. Colorimetrically, by means of sodium nitroprusside.
4. By means of double silver cyanide.

Numerous other methods might be used with suitable modifications to make them applicable to complex cyanide solutions. (See Fresenius, *Quant. Anal.*, 7th ed., Vol. I., pp. 380-390.)

Method No. 1.

Gravimetric Estimation of Sulphides by Means of Lead Salts.

An excess of carbonate of lead, or an alkaline lead salt such as a solution of oxide of lead (plumbate), or tartrate of lead in excess of caustic alkali is added to the cyanide solution, and the precipitate

of lead sulphide collected on a filter and washed. The precipitate is then oxidized by means of chlorine or bromine in presence of an excess of alkaline hydrate, filtered, and the solution acidified. The excess of chlorine or bromine is then boiled off, the sulphuric acid precipitated by barium chloride and determined in the usual way. The method is stated to be accurate but tedious.

Method No. 2.

Precipitation by Means of Lead Salts and Conversion into Thiocyanate.

This method is described by Feldtmann and Bettel (*Proceedings* Chem. and Met. Soc. South Africa, Vol. I., pp. 267-273). It is based on the fact that lead sulphide is decomposed by alkaline cyanides on exposure to bright sunlight, or in presence of hydrogen peroxide, with conversion of the sulphur into thiocyanate. The latter may then be estimated by one of the methods described above (*e.g.*, by titration of the acidulated solution with N/100 permanganate), and the amount of sulphide found by calculation.

The method is as follows:

The solution is agitated with a slight excess of precipitated lead carbonate and filtered. The precipitate, consisting of lead carbonate and sulphide, is transferred to a flask and covered with a few c.c. of a solution of potassic or sodic cyanide free from sulphides, sulphocyanides or ferrocyanides. This is best prepared from pure potassic or sodic hydrate and pure hydrocyanic acid. A slight excess of hydrogen peroxide is then added, about 3 or 4 times as much as is necessary to whiten the precipitate, and allowed to act for from 10 to 15 minutes. A small quantity (say half a gram) of manganese dioxide is added, and the mixture agitated for about two minutes to destroy the excess of hydrogen peroxide.

$$H_2O_2 + 2MnO_2 = H_2O + Mn_2O_3 + O_2.$$
$$Mn_2O_3 + H_2O_2 = H_2O + 2MnO_2.$$

The solution is then filtered off, acidified with sulphuric acid, and titrated with N/100 permanganate.

1 c.c. N/100 $KMnO_4$ = 0.00005345 gram S.
= 0.00018345 gram K_2S.
= 0.00016193 gram KCNS.

The same conversion may be effected without the use of hydrogen peroxide by merely exposing the mixture of lead sulphide and pure cyanide to bright sunlight for several hours.

Method No. 3.

See Appendix, page 176.

Colorimetric Estimation of Sulphides by Means of Sodium Nitroprusside.

This method, devised by Dr. J. Loevy of Johannesburg, is very rapid and simple. The solutions required are:

(*a*) Standard sodium sulphide: 40 grams Na_2S and 0.2 gram NaOH dissolved to a liter. 1 c.c. of this solution = 0.01643 gram S.

(*b*) Standard zinc sulphate: 43.82 grams $ZnSO_4 \cdot 7H_2O$ per liter. 1 c.c. = 0.01 gram Zn.

(*c*) Sodium nitroprusside: 5 grams of the salt dissolved in 100 c.c. water, to which 4 to 6 drops of 5 per cent cyanide are added.

For the estimation of sulphides in samples of commercial cyanide the method is carried out as follows:

A. Ten grams of the cyanide to be examined are dissolved in water and made up to 500 c.c. Of this solution, 100 c.c. are placed in a cylinder.

B. Ten grams of cyanide free from sulphides is also dissolved to 500 c.c. and 100 c.c. placed in another similar cylinder.

One c.c. of the nitroprusside solution is then added to each cylinder, which gives an intense violet color when sulphides are present. The standard sulphide solution (*a*), diluted in the proportion 1 : 10, is now added drop by drop to the cylinder *B* (containing pure cyanide) until the tint is the same in each.

The sodium sulphide solution is standardized by means of the zinc solution (*b*), using filter paper dipped first in ferric chloride, then in very dilute ammonia as an indicator.

[I find that this may be done much more easily, and probably more accurately, by making use of the method (No. 4) described below.]

1 c.c. zinc solution = 0.00488 gram sulphur.

Preparation of Sodium Nitroprusside.—Concentrated nitric acid is diluted with its own volume of water. This diluted acid is mixed with powdered potassium ferrocyanide in the proportion:

2 parts $K_4FeCy_6 \cdot 3H_2O$,
5 parts diluted HNO_3.

The salt dissolves to a coffee-colored liquid evolving CO_2, N, CN and HCN. It is warmed on a water bath until the liquid gives a dark green or slate colored precipitate instead of a blue precipitate with ferrous sulphate. It is then cooled, neutralized with sodium carbonate and filtered.

Method No. 4.

Estimation of Sulphides by Adding Double Cyanide of Silver and Titrating the Free Cyanide Liberated.

On adding an excess of a solution of the double cyanide of silver to a liquid containing alkaline sulphides, free cyanide is produced in proportion to the amount of sulphide present, thus:

$$2KAgCy_2 + K_2S = Ag_2S + 4KCy.$$

After filtering off the precipitated sulphide of silver, the cyanide is estimated by adding potassium iodide and titrating in the ordinary way with silver nitrate.

Any cyanide originally present in the liquid must be separately determined after treatment with lead carbonate, and the amount deducted from that previously found.

For rapid approximate results, the solution, after addition of the silver double cyanide and thorough agitation, may be made up to a definite volume, and an aliquot part filtered off for titration. The silver sulphide generally settles rapidly and is easily filtered; a little lime may, however, be added with advantage, in some cases.

The results obtained in numerous tests with this method were strictly proportional to the amount of sulphide present.

The silver double cyanide is prepared by adding silver nitrate to a solution of, say, 0.5 per cent KCy until a slight permanent turbidity is formed, allowing to stand for some time, and filtering.

See Appendix, page 178.

SECTION E.

Other Reducing Agents.

Estimation of Nitrites.—The presence of nitrites may be detected by the liberation of iodine when potassium iodide is added

to a solution slightly acidulated with sulphuric acid. Cyanides, ferrocyanides and thiocyanates do not interfere, but ferricyanides must be absent, as they give the same reaction. The haloid compounds of cyanogen also decompose potassium iodide in the same way.

Nitrites also reduce permanganate, and would be determined along with thiocyanates, etc., in the processes described above.

They may be estimated in cyanide solutions by the iodometric method of Dunstan and Dymond (*Phar. Journ.* [3] XIV., p. 741, and Sutton, *Volum. Anal.,* 8th ed., p. 292), which depends on the reaction with potassium iodide just described. The operation must be conducted in absence of air, and the solution of potassium iodide and sulphuric acid must be boiled to expel air and any traces of free iodine before admitting the cyanide solution in which the nitrite is to be estimated. When the reaction is complete, the liberated iodine is determined in the usual way by standard thiosulphate with or without starch indicator.

The potassium iodide and sulphuric acid (10 per cent solution) are first boiled in a flask provided with a funnel connected by means of a piece of rubber tubing and a screw clamp, so that it may be closed air-tight as soon as all air has been expelled and steam is issuing from the flask. The liquid to be examined is then introduced through the funnel by opening the clamp cautiously, and the funnel is then washed with water free from air. The thiosulphate solution may be admitted through the funnel in the same way.

The reactions occurring are:

(*a*) $H_2SO_4 + 2KI = K_2SO_4 + 2HI$.

(*b*) $H_2SO_4 + 2KNO_2 = K_2SO_4 + 2HNO_2$.

(*c*) $2HI + 2HNO_2 = 2H_2O + 2NO + I_2$.

See Appendix, page 183.

CLASS IV.

AUXILIARY AGENTS.

General Remarks.—We shall include under this heading any substance which hastens the rate of solution of the precious metals by cyanide, or which causes the extraction of these metals from compounds which would not otherwise be attacked.

From what has already been said, it is evident that oxygen, or any substance capable of supplying oxygen directly or indirectly to the solution, is in this sense, under ordinary circumstances, an auxiliary agent. There are also some other substances which do not contain oxygen, and which do not, at all events, act directly as carriers of oxygen, which nevertheless exert a marked influence in increasing the rate of solution.

We shall here consider:

A. Oxygen.
B. Active Haloids.
C. Peroxides.
D. Ferricyanides.

SECTION A.

Estimation of Oxygen.

A correct determination of the amount of free oxygen or its equivalent would be of the greatest value in determining the efficiency of a cyanide solution. Unfortunately no method has so far been suggested which does not involve more or less complicated operations and delicate manipulations. Two methods have been proposed for determining the amount of free oxygen in cyanide solutions, both of them based upon well-known processes for the determination of dissolved oxygen in water. These are:

1. The gasometric method, based on that of Lunge and Schmidt (*Zeitschrift f. Anal. Chem.*, Vol. XXV., p. 309).

2. The iodometric method, based on Thresh's process.

Method No. 1.

Estimation of Oxygen by Process Based on the Gasometric Method of Lunge and Schmidt.

An account of this process is given by Bettel (*Proceedings* Chem. and Met. Soc. South Africa, Vol. I., p. 276), its application to cyanide solutions being based on the assumption that the dissolved oxygen is expelled without appreciably attacking the cyanide or the impurities contained in the solution when the latter is boiled at 80° C. under reduced pressure for about 15 minutes. This does not apply to sulphides, which must be removed before making the test.

The process is identical with that described in Sutton's *Volumetric Analysis* (8th ed., p. 613), where full details are given as to the apparatus and manipulations required. It involves the use of a nitrometer, consisting of a graduated tube or burette connected at the upper end by means of a two-way cock with a small funnel and with a side tube, which can be joined by rubber tubing with the flask containing the solution to be examined.

When the method is applied to cyanide solutions, the temperature and specific gravity of the liquid must be taken for the purposes of calculation.

When sulphides are present, carbonate of lead is added, suspended in a few c.c. of the liquid, and allowed to settle in a bottle filled to the neck. The clear liquid is then used.

The gases present will be nitrogen, oxygen, and traces of ammonia. If hydrocyanic acid is found in the liquid before boiling, ammonic cyanide vapor may be present in the collected gases.

Before collecting the gases, about 1 c.c. of caustic potash solution is admitted to the nitrometer, and mixed with the condensed water in the collecting tube of the same. The gas is then transferred to the second nitrometer, which contains a drop of sulphuric acid. This absorbs the ammonia. The gas, now cooled and measured, consists of nitrogen and oxygen; it is transferred to a third nitrometer, containing alkaline pyrogallate. After the oxygen is absorbed, the residual nitrogen is transferred to the measuring nitrometer, cooled, and the volume, etc., noted. The loss in volume is then calculated to normal temperature and pressure, from which is deduced the

number of c.c. oxygen at normal temperature (0° C.) and pressure (760 mm.) per liter of cyanide solution.

Bettel states that the following decompositions occur when cyanides and cyanates are boiled under the conditions of the test:

(1) $MCN + 2H_2O = MHCO_2 + NH_3$.

(2) $2MCNO + 4H_2O = M_2CO_3 + (NH_4)_2CO_3$.

He also says that the dissolved oxygen does not perceptibly attack the formates, sulphocyanides, ferrocyanides, nickel, cobalt, copper and zinc compounds in solution.

Method No. 2.

Estimation of Oxygen by a Modification of Thresh's Iodometric Method.

This method is fully described by A. F. Crosse (*Journal* Chem. and Met. Soc. South Africa, 1899, pp. 107-112). See also, for details of Thresh's process, Sutton (*Volum. Anal.*, 8th ed., pp. 305-310) and *Journal* Chem. Soc. (Vol. LVII., p. 185).

It is based on the fact that when potassium iodide and a nitrite are added to water, which has been acidulated with sulphuric acid, iodine is liberated in addition to the amount due to the reaction:

(*a*) $H_2SO_4 + KI + KNO_2 = K_2SO_4 + H_2O + NO + I$,

this additional decomposition arising as follows:

(*b*) $3H_2SO_4 + 4KI + 2KNO_2 + O = 3K_2SO_4 + 3H_2O + 2NO + 2I_2$.

From these reactions it will be seen that 16 parts of oxygen liberate 2×126.92 parts of iodine (deducting the iodine due to reaction *a*).

The solutions required are:

1. Combined nitrite and iodide solution consisting of:
   Sodium nitrite, 0.5 gram;
   Potassium iodide, 20 grams;
   Distilled water, 100 c.c.
2. Dilute sulphuric acid:
   Pure concentrated H_2SO_4, 1 part;
   Distilled water, 3 parts.
3. Clear fresh solution of starch.
4. Sodium thiosulphate, 7.757 grams in 1 liter; 1 c.c. corresponds to 0.25 milligram of oxygen.
5. Zinc sulphate, 200 grams $ZnSO_4.7H_2O$ per liter.

6. Bromine water, consisting of
   Bromine, 1 part;
   Water, 2 parts.

The operation is conducted in an atmosphere free from oxygen, *e.g.*, of coal gas. This may be conveniently arranged by using a wide-mouthed jar of about 500 c.c. capacity, closed by a rubber stopper having four perforations: two of these are for the entrance and exit of the gas, one to receive a separating funnel through which the solution to be tested is introduced, after addition of the necessary reagents, and the fourth to admit the thiosulphate solution for titrating the liberated iodine.

The separating funnel has a stopper at the upper and a tap at the lower end, and its capacity must be accurately determined.

Preliminary Tests.—In the method as modified by Crosse the solution is first prepared by removal of all cyanides and absorbents of iodine. For this purpose the solution to be examined is first treated with zinc sulphate. A bottle capable of holding 2½ liters of the liquid to be tested is carefully filled and well stoppered, its exact capacity being known.

Test for Zinc Required to Precipitate Cyanide.—One hundred c.c. are withdrawn from the large bottle and titrated with the zinc sulphate solution (No. 5 above), using phenol phthaleïn as indicator, until the tint is just destroyed. The calculated quantity of zinc sulphate is then added to the large bottle (without admitting air), the contents well shaken and allowed to settle.

Test for Iodine Absorbents.—A quantity of the prepared solution (siphoned off without allowing access of air) is mixed with a little of the dilute sulphuric acid (No. 2) and a few drops of potassium iodide and starch. Dilute bromine water (No. 6) is added until a blue color is obtained.

Test for Oxygen.—The separating funnel is now filled with the prepared solution. The same amount of sulphuric acid (say, 0.9 c.c. for 300 c.c. of solution), as in the previous test, and the amount of bromine water shown to be necessary, are now introduced and mixed by closing the stopper and turning the vessel over several times. Next, 1 c.c. of the nitrite and iodide solution (No. 1) are introduced, and the stopper immediately replaced. The lower end of the funnel is now inserted through the stopper of the wide-mouthed jar described above, which has previously been connected with the gas supply and with the burette containing the standard thiosulphate.

The apparatus is filled with gas and allowed to remain at rest for 15 minutes. The stopper of the funnel is then opened, and the tap turned so that the mixture is allowed to run into the jar. The thiosulphate is now run in slowly through a tube drawn out to a rather fine point, and connected at its upper end, by means of rubber tubing, with the burette from which the standard thiosulphate (No. 4) is delivered. When the color of the iodine is nearly discharged, starch solution is introduced through the funnel, and the titration continued. At first the color, after being completely discharged, returns on standing for a few seconds.

Correction for Nitrites in Solution and Reagents Used.—In cases where nitrites are present the process is altered as follows: Add potassium hydroxide and then zinc sulphate; determine the thiosulphate required by Thresh's method with clear solution after settlement and decantation; make a qualitative test for nitrites by acidifying a little of the clear solution with dilute sulphuric acid and adding potassium iodide and starch, and finally apply a correction for the nitrites and reagents used. The test required for this correction is as follows: "Pour into a very strong 350 c.c. flask a quantity of solution equal to that used in the experiment (say, 293 c.c.), add a few drops of KOH and close the flask with a rubber stopper having one perforation, through which is passed a glass tube with a glass stop-cock. Boil the solution for a few minutes and close the stop-cock. Cool the flask, and when cold pour the liquid into the funnel of Thresh's apparatus, add 1 c.c. of the iodide and nitrite solution and 1 c.c. of sulphuric acid (1:1). Allow to stand for 10 minutes and titrate in an atmosphere of coal gas, as previously described." The quantity of thiosulphate required gives the correction for nitrites and for the reagents, as the same amounts of reagents are used in both tests.

Simplified Process.—The following simplified method is described by A. F. Crosse (*Journal* Chem. and Met. Soc. South Africa, Vol. III., p. 4). A solution is prepared containing potassium iodide, 20 grams, potassium nitrite, 2 grams, made up to 100 c.c.

The cyanide solution to be tested is siphoned into the separating funnel without previous treatment with zinc sulphate, then 1 c.c. of the above iodide and nitrite solution is added, and 3 c.c. of sulphuric acid (1:1). After shaking up and allowing to stand for 15 minutes, titrate as before described, in an atmosphere of coal gas, with the same thiosulphate solution (No. 4 above). There is no

visible liberation of iodine, as the colorless iodide of cyanogen is produced in proportion to the free oxygen plus the quantity due to the reagents. This substance may, however, be titrated with thiosulphate and starch.

The correction for nitrites in reagents, etc., is made as follows:

Take about 400 c.c. of the solution, and add 0.3 gram pure ferrous sulphate and the same weight of caustic lime; shake up well and filter into a flask through which coal gas is passing. The precipitated ferrous hydrate absorbs all free oxygen, so that any iodine liberated on testing the filtrate, as before, will be due to the reagents alone.

SECTION B.

Estimation of Active Haloids.

The metallic compounds of the haloid elements, such as the chlorides, bromides and iodides of the alkali metals, exert little or no beneficial effect on the extraction of the precious metals by cyanide; but it is well known that the haloid elements themselves, when added in suitable proportions to a cyanide solution, form compounds which accelerate the rate of solution to a remarkable degree. Since the use of bromide of cyanogen in conjunction with potassium cyanide has been adopted to some extent, as in the Sulman-Teed and Diehl processes, we shall describe a method for estimating this body in presence of cyanides, etc.

Estimation of Cyanogen Bromide.—On adding a few drops of concentrated hydrochloric acid, this compound is decomposed as follows:

$$BrCy + HCl = HCy + ClBr.$$

If now we add an excess of potassium iodide, a liberation of iodine occurs as follows:

$$ClBr + 2KI = KCl + KBr + I_2;$$

or, expressing both changes in one equation:

$$BrCy + HCl + 2KI = HCy + KCl + KBr + I_2.$$

Hence 52.965 parts of bromide of cyanogen liberate 126.92 parts of iodine.

The free iodine may be estimated in the ordinary way by standard thiosulphate and starch:

UNIV. OF CALIFORNIA

1 c.c. N/10 thiosulphate = 0.0052965 gram BrCy.

$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$.

The reaction in the case of chloride of cyanogen would presumably be:

$$ClCy + HCl + 2KI = HCy + 2KCl + I_2.$$

The presence of free cyanides does not interfere, as the hydrocyanic acid liberated does not absorb iodine in presence of excess of hydrochloric acid.

It must be remembered that many other oxidizing agents, *e.g.*, ferricyanides, peroxides, persulphates, and also nitrites, decompose potassium iodide under similar conditions, so that when these are present the test will not give correct results.

SECTION C.

Estimation of Peroxides.

Method No. 1.

By Liberation of Iodine.

In the absence of other oxidizing agents the peroxides of sodium and hydrogen may be estimated by acidifying pretty strongly with sulphuric acid, adding excess of potassium iodide, allowing to stand for about 5 minutes, and titrating the liberated iodine with N/10 or N/100 thiosulphate and starch.

1 c.c. N/10 thiosulphate = 0.0017 gram H_2O_2.
= 0.0039 gram Na_2O_2.

The reactions are:

$$H_2SO_4 + 2KI = K_2SO_4 + 2HI.$$
$$2HI + H_2O_2 = 2H_2O + I_2.$$

Where the peroxide of an alkali metal is present, it, of course, yields hydrogen peroxide on acidifying.

Method No. 2.

By Titration with Permanganate.

Where interfering substances are absent, we may estimate peroxides by means of the following reaction; the solution must be diluted considerably if much peroxide is present:

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 =$$
$$K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

A more exact method is to add an excess of permanganate, and determine the excess by standard oxalic acid.

SECTION D.

Estimation of Ferricyanides.

Ferricyanides rarely occur in ordinary working solutions. They have sometimes been used, however, as aids to extraction, and may occasionally be formed by the reactions taking place during treatment.

1. When other oxidizing agents are absent, they may be determined by liberation of iodine from potassic iodide.

2. When reducing agents are absent, they may be determined, after reduction to ferrocyanide, by titration with permanganate. This reduction may be performed: (*a*) by ferrous sulphate in presence of excess of alkali; (*b*) by sodium peroxide; (*c*) by sodium amalgam.

3. By titration with copper sulphate or nitrate, using ferrous sulphate indicator. (See p. 82.)

Method No. 1.

Estimation of Ferricyanides by Liberation of Iodine.

This method was originally described by E. Lenssen (*Ann. der Chem. u. Pharm.*, 105, 62), and improved by C. Mohr (see also Fresenius, *Quant. Anal.*, 7th ed., Vol. I., p. 379, and Sutton, *Volum. Anal.*, 8th ed., p. 227).

It is carried out as follows: A measured quantity of the solution is taken, potassium iodide crystals added, together with hydrochloric acid in tolerable quantity; then a solution of pure zinc sulphate in excess. After standing for a few minutes, till the decomposition is complete, the excess of acid is neutralized by bicarbonate of soda in slight excess. The liberated iodine may then be titrated with N/10 thiosulphate and starch, with great exactness. The reaction is as follows:

$$K_3FeCy_6 + KI = K_4FeCy_6 + I.$$

The ferrocyanide thus formed is precipitated, on addition of zinc sulphate, as ferrocyanide of zinc.

Free cyanides appear to interfere slightly with the reaction, rendering the results somewhat too low.

Method No. 2.

Estimation of Ferricyanides by Reduction to Ferrocyanides and Titration with Permanganate.

Ferrocyanides, thiocyanates, etc., must be absent, or, if present, their amount must be determined by a separate experiment and allowed for.

(*a*) *Reduction with Ferrous Salt.*—According to Sutton (*Volum. Anal.*, 8th ed., p. 227), the reduction is best performed by boiling with an excess of caustic alkali and adding small quantities of concentrated solution of ferrous sulphate until the precipitate which occurs possesses a blackish color (signifying that the magnetic oxide is formed):

$$3Fe(OH)_2 + 2K_3FeCy_6 + 2KOH = 2K_4FeCy_6 + Fe_3(OH)_8.$$

The solution is diluted if necessary, filtered through a dry filter, and an aliquot part acidulated with sulphuric acid and titrated as described under ferrocyanides.

(*b*) *Reduction with Peroxides.*—Another method consists in boiling with excess of potash, then cooling and adding hydrogen peroxide till the color is yellow,

$$2K_3FeCy_6 + 2KOH + H_2O_2 = 2K_4FeCy_6 + 2H_2O + O_2,$$

or heating with sodium peroxide till the effervescence ceases, boiling off excess of peroxide, acidifying with sulphuric acid, cooling, and titrating with permanganate. (Kassner, *Arch. Pharm.*, 232, 226.)

(*c*) *Reduction with Sodium Amalgam.*—Bettel (*Proceedings* Chem. and Met. Soc. South Africa, Vol. I., p. 168) recommends allowing sodium amalgam to act for 15 minutes on the solution in a narrow cylinder, then estimating the ferrocyanide formed, of course, deducting ferrocyanide and thiocyanate originally present.

CLASS V.

INACTIVE BODIES.

General Remarks.—In addition to the active cyanogen compounds and various substances which either promote or interfere with their action in the treatment of ores, there are a number of substances which appear to have little or no influence on the result. They may arise as impurities in the commercial cyanide used, or may be derived from the material treated.

Among the many substances of this class which may occur, the following will be here considered:

1. Cyanates and isocyanates.
2. Chlorides.
3. Nitrates.
4. Sulphates.
5. Silicates.

SECTION A.

Estimation of Cyanates and Isocyanates.

Salts of cyanic acid appear to be almost invariably present in samples of commercial cyanide. They exist in two isomeric forms, probably corresponding to different molecular formulæ, as follows:

Cyanates, R — O — C≡N.

Isocyanates, R — N = C = O.

They exhibit the following difference in properties; whereas the alkaline cyanates are not precipitated by silver nitrate, the isocyanates are completely precipitated, thus:

$$KNCO + AgNO_3 = AgNCO + KNO_3.$$

Method No. 1.

By Precipitation with Silver Nitrate and Chromate Indicator.

The reaction given above is the basis of the following method, described by Feldtmann and Bettel (*Proceedings* Chem. and Met.

Soc. of South Africa, Vol. I., p. 272). It only serves for the estimation of isocyanates.

If to a solution containing cyanide, isocyanate, sulphocyanide, ferrocyanide, chloride, carbonate and bicarbonate we add nitrate of silver in excess, we get a precipitate consisting of silver cyanide, silver isocyanate (carbimide), silver sulphocyanide (thiocyanate), silver ferrocyanide, silver chloride, silver carbonate.

By adding cold carbonic acid water to the solution, the alkaline carbonate is converted into bicarbonate, which does not produce a precipitate with silver nitrate.

Having estimated chlorides, cyanides, sulphocyanides and ferrocyanides, and determined their precipitation-value in terms of c.c. of silver nitrate solution (one need hardly remark that sulphides, if present, are first removed from solution by lead carbonate), the actual titration for isocyanates is now performed after addition of excess of carbonic acid water and two drops of chromate of potash (see Vielhaber's method for cyanide, above).

The chromate solution should be added only after the reaction with silver nitrate is nearly complete. A little care is necessary in judging the change of color, a comparison solution tinted with chromate being used as a guide to the end reaction. According to Bettel and Feldtmann, the titration must further be made in ice-cold water, as the isocyanate appears to decompose pretty rapidly at ordinary temperatures, being probably converted into the normal cyanate, which, as before stated, is not precipitated by nitrate of silver.

The presence of ferrocyanides, thiocyanates, chlorides, etc., does not interfere, but their equivalent in c.c. of silver solution must be deducted from the number obtained in titrating for isocyanate.

Using a solution containing 13.0464 grams $AgNO_3$ per liter, the silver-equivalents (for complete precipitation) will be as follows:

$$1 \text{ c.c. standard } AgNO_3 = \begin{cases} 0.005 \text{ gram KCy.} \\ 0.00707 \text{ gram } K_4FeCy_6. \\ 0.00746 \text{ gram KCNS.} \\ 0.00623 \text{ gram KNCO.} \\ 0.002723 \text{ gram Cl.} \end{cases}$$

Method No. 2.

Estimation of Cyanates by Differential Method, Using Silver Nitrate with and without Addition of Nitric Acid.

The following method, due to E. Victor (*Zeitschrift f. Anal. Chem.*, 1901, 40 [7] 462-465; see also *Journal* Soc. Chem. Ind., Vol. XX., p. 1031), is based on the fact that silver nitrate precipitates cyanide and cyanate completely in neutral solution, but only cyanide in presence of nitric acid, silver cyanate being readily soluble in that acid.

An approximately 10 per cent solution of the sample of commercial cyanide is prepared, and of this, two portions of 10 c.c. each are measured into 100 c.c. flasks, to each of which a known excess of N/10 $AgNO_3$ is added. One lot is then diluted to the mark, filtered, and the excess of silver titrated in an aliquot portion of the liquid after acidification with HNO_3, by N/10 ammonium thiocyanate, using ferric alum as indicator (*i.e.*, by Volhard's method). The total cyanide and cyanate is thus found. To the other portion 10 c.c. of dilute nitric acid is added, the liquid diluted to 100 c.c., filtered, and the excess of silver titrated as before.

The silver consumed corresponds to the cyanide in the solution. [If ferrocyanides, thiocyanates or chlorides were originally present they would not interfere, as they would affect both titrations equally.]

Carbonates, if present, must be decomposed by addition of barium nitrate before proceeding as above. [According to W. J. Mellor (see below) barium nitrate cannot be used on account of the insolubility of barium cyanate, and calcium nitrate, free from chlorides, is recommended.]

The author refers to the process of Feldtmann and Bettel, given above, according to whom: (*a*) Only isocyanate and not normal cyanate, gives an insoluble silver salt; (*b*) an isocyanate, in solution is rapidly transformed into normal cyanate at quite low temperatures (*e.g.*, 25° C.).

For these reasons they (Feldtmann and Bettel) insist that the solution of the sample and the precipitation with silver nitrate must be effected at a temperature near 0° C. in order to avoid loss of isocyanate.

E. Victor has examined these statements experimentally, and

finds that a solution of alkaline isocyanate does not change sensibly at 25° C. in three hours. Only after 24 hours' standing a diminution of about 30 per cent had taken place, the loss being due not to conversion of isocyanate into normal cyanate, but to the well-known decomposition of the iso-salt into ammonia and potassium carbonate:

$$KNCO + 2H_2O = KHCO_3 + NH_3.$$

In any case there is no necessity to operate at such inconveniently low temperatures.

The reaction of nitric acid on silver cyanate appears to be

$$AgCNO + 2HNO_3 + H_2O = AgNO_3 + NH_4NO_3 + CO_2.$$

See Appendix, page 181.

Method No. 3.

Estimation of Cyanate by Means of Acid Required to Dissolve Silver Cyanate.

A method very similar to the preceding is given by J. W. Mellor (*Zeitschrift f. Anal. Chem.*, 1901, 34 [1] 17-21 and *Journal* Soc. Chem. Ind., Vol. XX., p. 284; see also Allen *Comm. Org. Anal.*, Vol. III., p. 484).

1. Twenty grams of the commercial cyanide are dissolved in about 100 c.c. of water (or a convenient volume of solution is measured out), and the carbonates precipitated by calcium nitrate free from chlorides. Barium nitrate cannot be used, as barium cyanate is insoluble. The precipitate is filtered off, washed, and the filtrate and washings made up to 200 c.c. (*A*) One c.c. of solution = 0.1 gram of commercial cyanide.

2. Ten c.c. of the solution (*A*) are treated with excess of ammonia solution and a few drops of KI, and titrated for cyanide in the ordinary manner with silver nitrate.

3. To about 10 c.c. of the solution (*A*), silver nitrate is added until no further precipitation takes place. The precipitate, consisting of a mixture of silver cyanide and silver cyanate, is collected on a filter and washed with ice-cold water.

It is then heated to about 50° C. with about 5 c.c. of normal nitric acid, which decomposes the whole of the cyanate. The filtrate is titrated with normal sodium hydroxide. Assuming n c.c to be required, 1 gram of original sample would contain $0.0405\ (5 - n)$ gram KCNO.

According to O. Herting (*Journal* Soc. Chem. Ind., Vol. XX.)

the temperature of 50° C. is insufficient; he states that more reliable results are obtained by digesting on a water bath with the nitric acid for at least an hour.

Method No. 4.

Estimation of Cyanates by Determination of Nitrogen.

O. Herting (*Zeitschrift f. Angew. Chem.*, 1901 [24], 585-586) recommends the following method, based on the facts that cyanides are decomposed by acids with evolution of HCy and formation of salts of the metal, whereas cyanates are decomposed according to the equation:

$$RCNO + 2HCl + H_2O = RCl + NH_4Cl + CO_2.$$

In making a determination, from 0.2 to 0.5 gram of the commercial cyanide is dissolved in a few c.c. of water, and the solution evaporated with HCl or H_2SO_4 on the water-bath. The residue is dissolved in water, and the nitrogen in the solution is determined as NH_3 by distillation with sodium hydroxide and calculated as KCNO. (See estimation of ammonia, above.)

See Appendix, pp. 179, 183.

Qualitative Test for Cyanates.—Small quantities of cyanate may be detected in potassium cyanide by the use of cobalt acetate. This gives an intense blue color, forming a compound which crystallizes as $Co(CNO)_2 + 2KCNO$.

The cyanide is dissolved in a minimum quantity of water, absolute alcohol added to precipitate most of the KCy, then carbonic acid is passed into the remaining liquid for, say, 45 minutes, the K_2CO_3 formed is filtered off, and the filtrate tested with cobalt acetate (*Engineering and Mining Journal,* Vol. LX., p. 489).

SECTION B.

Estimation of Chlorides.

The estimation of chlorides in cyanide solutions may be made in several ways, most of which involve precipitation as silver chloride. The following will be here considered:

1. Precipitation with silver nitrate and chromate indicator, making corrections for cyanogen compounds.

2. Precipitating cyanide and chloride together as silver salts, and determining the former in the precipitate by organic analysis.

3. Precipitating cyanide and chloride together with silver, decomposing with sulphuric acid and zinc, and estimating chlorine in the liquid.

4. Decomposing silver precipitate by fusion with carbonate of soda and niter.

5. Evaporating with nitric acid, and fusing residue with sodium carbonate and niter.

Method No. 1.

Estimation of Chlorides by Direct Precipitation with Silver Nitrate.

This is merely an application of Mohr's well-known volumetric method of estimating chlorides, and has been already described under total cyanogen. The other constituents of the solution, which are precipitated by silver nitrate before the chromate reaction occurs, must be separately determined, and their equivalents in c.c. of standard silver nitrate solution deducted from the result of the titration. Carbonates may be removed by preliminary treatment with carbonic acid water, as in Bettel and Feldtmann's method for cyanates (see above), or the protective alkali may be neutralized by cautious addition of dilute nitric acid.

It must be remembered that free cyanides are completely precipitated as AgCy, using twice as much $AgNO_3$ as would be required to give a permanent turbidity, and that ferrocyanides and thiocyanates are completely precipitated as silver salts before the chromate reaction occurs.

Using a solution containing 13.039 grams $AgNO_3$ per liter, the silver equivalents for complete precipitation will be as follows:

$$1 \text{ c.c. standard } AgNO_3 = \begin{cases} 0.005 \text{ gram KCy.} \\ 0.002723 \text{ gram Cl.} \\ 0.004489 \text{ gram NaCl.} \\ 0.005726 \text{ gram KCl.} \end{cases}$$

Method No. 2.

Estimation of Chlorides by Precipitating with Cyanides, as Silver Salts, and Decomposing Precipitate to Determine Cyanides.

This method is given by Fresenius (*Quant. Anal.*, 7th ed., Vol. I., p. 512) as follows:

Precipitate with solution of silver, collect the precipitate upon a weighed filter, and dry on the water bath until the weight remains constant; then determine the cyanogen by the method of organic analysis (*e.g.*, by heating with copper oxide or lead chromate in a combustion tube and collecting the nitrogen evolved over mercury and caustic potash, or by conversion into ammonia by distillation with soda lime. The chlorine is found by difference.

This method would require further modifications in presence of ferrocyanides, thiocyanates, etc., and in any case would, in general, be too tedious for use in the analysis of cyanide solutions.

Method No. 3.

Precipitation of Chloride and Cyanide Together as Silver Salts, Decomposing the Precipitate and Estimating Chlorine.

This method is given in Fresenius (*Quant. Anal.*, 7th ed., p. 512) and Allen (*Comm. Org. Anal.*, Vol. III., pt. 3, p. 431).

The cyanide and chloride are precipitated together as silver salts by adding excess of silver nitrate. The precipitate (xAgCy + vAgCl) is dried at 100° C. and weighed.

Then heat the precipitate, or an aliquot part of it, in a porcelain crucible, with cautious agitation of the contents, to complete fusion; cool, add dilute sulphuric acid to the fused mass, then reduce by zinc, filtering the solution from metallic silver and paracyanide of silver. The cyanides, ferrocyanides, thiocyanates, etc., will be entirely decomposed, and the whole of the chlorine will be present in the filtrate as chloride of zinc. In this liquid it may be determined by any of the ordinary gravimetric or volumetric methods. The results are said to be very satisfactory.

[Allen observes that small quantities of cyanide in a mixture with chloride are better determined as in the previous method, by igniting the precipitate with soda-lime or heating it with strong sulphuric acid, and determining the resultant ammonia.]

K. Kraut (*Zeitschrift f. Anal. Chem.*, 2, p. 243) decomposes the precipitate of silver cyanide and chloride, after weighing as above, by heating it, or an aliquot part of it, with nitric acid of sp. gr. 1.2 in a sealed tube at 100° C. for several hours, or at 150° C. for one hour. The cyanide of silver is completely decomposed, while the chloride is unaffected. Filter the contents of the tube, wash the precipitate, and weigh it as AgCl. The loss indicates the amount of AgCy.

Method No. 4.

Decomposition of Silver Precipitate by Fusion with Sodium Carbonate and Niter.

The solution is acidified with nitric acid, and precipitated with silver nitrate solution; the precipitate filtered and washed, then fused with 4 parts of sodium carbonate and 1 part potassium nitrate. The fused mass is extracted with water, and the chlorine determined in the solution by the ordinary gravimetric or volumetric methods. (See Fresenius, *Quant. Anal.*, 7th ed., Vol. I., p. 513.)

Method No. 5.

Estimation of Chlorides by Evaporation with Nitric Acid and Fusion of Residue with Sodium Carbonate and Niter.

Bettel and Feldtmann (*Proceedings* Chem. and Met. Soc. South Africa, Vol. I., p. 275) give the following method for determining chlorides in commercial cyanide: "A portion of the cyanide solution, equal to about 5 grams of the solid cyanide, is evaporated with sufficient nitric acid to form nitrates with the bulk of the potassium and sodium present, leaving about 50 to 100 milligrams of cyanide unattacked. When most of the hydrocyanic acid has escaped, about 5 grams sodium nitrate and 3 grams sodium carbonate are added, and intimately mixed with the partly decomposed cyanide solution, the evaporation continued to dryness, and then the residue gently ignited to decompose nitrates of iron, etc. The melt is now cooled, dissolved in water, and the insoluble oxides filtered off and washed. [The oxide of iron may then be estimated and calculated to ferrocyanide if required.] The filtrate from the insoluble oxides

is now acidulated with pure nitric acid, and the solution raised to boiling point; this decomposes cyanates with formation of ammonia and carbon dioxide. The chloride may now be estimated in the usual manner.

J. W. Mellor (*Zeitschrift f. Anal. Chem.*, 1901, 34 [1], 17-21) applies the same method, fusing the commercial cyanide direct, after weighing a suitable quantity, with a mixture of potassium nitrate and sodium carbonate (1:5), in a porcelain crucible. The mass is dissolved in boiling water, acidified with nitric acid, and the chlorides determined in the usual way. (See Appendix, p. 184.)

SECTION C.

Estimation of Nitrates.

The ordinary methods for the estimation of nitrates are somewhat complex and involve delicate manipulations. They are mostly based upon conversion into ammonia or ammonium salts by the action of strong acids and alkalis, with subsequent distillation and collection of the ammonia. As cyanide solutions contain various other substances capable of yielding ammonia under these conditions, the methods could not be directly applied. Probably most of the interfering substances could be removed by precipitating with a pure solution of acetate or sulphate of silver in slight excess. The filtrate might then be concentrated and distilled with the addition of strong caustic potash and a mixture of finely-divided zinc and iron. (See Sutton, *Volum. Anal.*, 8th ed., p. 274.)

SECTION D.

Estimation of Sulphates.

The estimation of sulphates is perhaps best made by the ordinary gravimetric method with barium chloride, after complete decomposition of the solution by evaporating several times to dryness with nitric and hydrochloric acids, finally with the latter alone. The

residue is diluted with distilled water, filtered, if necessary, a little pure hydrochloric acid added, heated nearly to boiling, and barium chloride added in slight excess. After standing several hours the precipitate is washed carefully by decantation several times with hot water, finally collected on a small filter, washed with hot water till free from chlorides, dried, gently ignited and weighed as $BaSO_4$. The precipitate must be ignited as far as possible apart from the filter paper. (For further details see Fresenius, *Quant. Anal.*, 7th ed., Vol. I., p. 299.)

W. J. Sharwood (*Engineering and Mining Journal*, 1898, p. 216) recommends adding excess of hydrochloric acid to the cyanide solution, heating till odor of hydrocyanic acid has disappeared and filtering off any zinc or copper ferrocyanides, Prussian blue or silver chloride that may be precipitated. Barium chloride may then be added to the filtrate without evaporation to dryness.

SECTION E.

Estimation of Silicates.

Soluble silicates of the alkali metals are decomposed by evaporation with nitro-hydrochloric acid, and gentle ignition of the residue. In some cases the insoluble residue, after this treatment, must be digested with ammonia and ammonium acetate in order to dissolve chloride of silver and sulphate of lead. The residue, which should be perfectly white, is then washed till no more traces of iron, etc., are found in the filtrate, dried, ignited and weighed as SiO_2.

CLASS VI.

NOBLE METALS.

General Remarks.—The correct estimation of the gold and silver contents of the solutions before and after precipitation is very essential, as a check on the extraction and as evidence of efficient precipitation. Some rapid method of making these estimations is much to be desired, but at present, for gold, at least, there is no accurate method which does not involve a fire assay.

We shall here describe:

(*A*) Methods in which gold and silver are determined together.

(*B*) Methods in which gold only is determined.

(*C*) Methods in which silver only is determined.

SECTION A.

Estimation of Gold and Silver Together.

A considerable number of methods have been suggested. These may be divided into the following groups:

(*a*) Those involving the evaporation of the entire quantity of solution taken for the test.

(*b*) Those in which copper salts are used as a precipitant.

(*c*) Those in which sulphuretted hydrogen is used as a precipitant.

(*d*) Those depending on reduction by other metals.

Group (a).—Estimation of Gold and Silver by Evaporation.

Method No. 1.

Evaporation with Litharge.

A measured volume of the liquid, varying according to the richness of the solution from, say, 30 c.c. up to 3 or 4 liters, is evaporated at a gentle heat in a porcelain basin without boiling. The solution may conveniently be measured on the assay-ton system. In

an ordinary case 10 A.T. or 291.6 c.c. would be a suitable quantity. Previous to evaporation, from 20 to 50 grams of litharge are sprinkled uniformly over the surface of the liquid. Some operators prefer to mix a little fine silica, or silica and charcoal, with the litharge. It is not advisable to add carbonate of soda, as this forms a very hard crust, difficult to remove from the dish. Towards the end of the evaporation care must be taken not to overheat the residue, as this might cause it to adhere too firmly.

When quite dry the residue is scraped out with a clean spatula, and mixed with a suitable flux, which may be varied according to circumstances. The following may be given as examples:

	(a)	(b)
Litharge (before evaporation)	30 grams.	45 grams.
Borax	20 "	10 "
Carbonate of soda	16 "	40 "
Silica	— "	25 "
Charcoal	0.5 "	1 "

The last portions remaining on the dish may be removed by means of a small piece of filter paper slightly moistened, the paper being afterwards added to the flux. If this fails to perfectly clean the dish, a drop or two of nitric acid is added.

The flux containing the dry residue, well mixed, is now transferred to a clay crucible and fused in an ordinary assay furnace. The fusion should be complete in 20 to 30 minutes. The charge is generally very fusible, giving a transparent, nearly colorless slag, but in other cases the slag may be stained owing to the presence of iron, copper and other impurities in the solution. The resulting lead button is then cupelled, keeping the temperature of the muffle, especially when silver is to be determined, at such a low temperature that feathers of litharge are formed on the cupel. The beads of gold and silver are then weighed and parted in the ordinary way.

This method, although somewhat long, is the most reliable and accurate which has so far been suggested. Duplicate assays give identical results when the operations are properly carried out.

Method No. 2.

Evaporation on Lead Foil.

For comparatively rich solutions it is sometimes convenient to determine the gold and silver contents by evaporating a weighed or

measured quantity in a small dish of lead foil, which may afterwards be rolled up and cupelled. Sometimes the lead containing the evaporated residue may be cupelled direct, but in other cases, owing to the presence of impurities, it is necessary to scorify. When poor solutions have to be assayed, large quantities of liquid must be taken, hence either larger dishes of lead foil or a number of small dishes must be used, the resulting lead buttons being afterwards run together and reduced in weight by scorification, thus increasing the labor and multiplying the chances of error. On the whole, except for very rich solutions, the method of evaporation with litharge is preferable.

Alfred James (*Cyanide Practice,* 1902) states that this method has a tendency to give low results.

Group (b).—Estimation of Gold and Silver by Means of Copper Salts.

Method No. 1.

Precipitation with Cuprous Chloride.

Prof. S. B. Christy has shown that gold and silver may be readily precipitated from cyanide solutions by means of cuprous chloride. It is advisable to remove the bulk of the free cyanide by first adding a slight excess of sulphuric or hydrochloric acid and boiling for some time. The solution used for precipitating is prepared by adding hydrochloric acid to a solution of copper sulphate and passing in sulphur dioxide, or by boiling the copper solution with sodium sulphite. On adding a little of this liquid to the hot acidulated cyanide solution a white precipitate is formed, consisting chiefly of cuprous cyanide, which carries down with it the greater part of the gold and silver. After allowing to settle, the clear liquid is poured off through a filter, the precipitate is then collected on the same filter, dried, scorified if necessary with grain lead, and cupelled. The resulting gold and silver bead is then weighed and parted.

It is advisable to test the filtrate, to make sure that cuprous chloride is in excess. This may be done by filtering a little of the liquid and testing with potassium ferrocyanide, which gives the characteristic reddish-brown precipitate of ferrocyanide of copper. The test may also be applied by absorbing a little of the liquid with filter paper and testing with a drop of ferrocyanide solution on a glass rod.

With fairly rich solutions the results are satisfactory, but the precipitation is not absolutely perfect, and gold and silver may always be found in the filtrate by evaporation with litharge.

A. Whitby (*Journal* Chem. and Met. Soc. South Africa, Vol. III., p. 15) applies the method as follows: To 700 c.c. of the cyanide solution add 25 c.c. of a 10 per cent solution of copper sulphate, then 5 to 7 c.c. concentrated hydrochloric acid, and lastly 10 to 20 c.c. of a 10 per cent solution of sodium sulphite. The precipitate, after vigorous shaking for about two minutes, is filtered off and run down with flux in the ordinary way. Assays can be completed in three hours, and results compare well with the evaporation test. With slimes solutions, which are normally weak in cyanide, it is better to add some cyanide before making the test.

See Appendix, pages 185, 187.

METHOD NO. 2.

Precipitation with Cupric Sulphate.

The following method is given by Walter H. Virgoe (*Proceedings* Inst. Min. and Met., Vol. X., p. 115):

To a liter of the cyanide solution add excess of cupric sulphate and acidify with hydrochloric, nitric or sulphuric acid; the precipitate, which is white and flocculent, contains all the gold and silver, and the bluish or greenish color of the filtrate indicates that excess of the copper sulphate has been added. The precipitate is washed, dried and placed in a scorifier with metallic lead. The results are accurate, and the whole operation can be done within an hour and a half.

The theory of the method may be expressed thus:

$$2AuKCy_2 + Cu_2Cy_2, 2KCy + 2H_2SO_4 = Au_2Cu_2Cy_4 + 2K_2SO_4 + 4HCy.$$

In a subsequent discussion on this method by the Chemical and Metallurgical Society of South Africa, A. F. Crosse recommended it, but preferred to fuse in a crucible with litharge, instead of scorifying. A. Whitby (*Journal* Chem. and Met. Soc. South Africa, Vol. III., p. 15) found, however, that all the gold is not precipitated by copper sulphate with addition of mineral acid, but that an additional precipitate is obtained by mixing sodium sulphite with the filtrate, the remainder of the gold being quantitatively recoverable from this precipitate. He therefore suggests the slight modification of Christy's method given above. (See Appendix, page 188.)

Group (c).—Estimation of Gold and Silver by Precipitation with Sulphuretted Hydrogen.

Henry Watson (*Engineering and Mining Journal,* 1898, p. 753) gives the following method, which is stated to be quick, accurate and economical:

"A pint or half a pint of the cyanide liquor is acidified with HCl, and heated to boiling. Add a solution of 2 grams of lead acetate, and then pass in a current of sulphuretted hydrogen gas until all the lead is precipitated as sulphide. Allow the solution to cool down somewhat, so as to thoroughly saturate it with H_2S. The gold will be precipitated with, and collected by, the lead sulphide. Filter off the precipitate and dry. Fuse and scorify the residue and cupel the resulting lead button."

I may remark that I tested a very similar method many years ago, but did not find the results at all satisfactory, being invariably lower than those obtained by evaporation.

Group (d).—Estimation of Gold and Silver by Reduction Method.

Precipitation with Sodium Amalgam.

Sodium amalgam, when shaken in a stoppered cylinder with a cyanide solution containing the precious metals, decomposes the double cyanides of these metals, the gold and silver amalgamating with the mercury. This is then collected and carefully distilled at a gentle heat. It is best to cupel the residue.

This method does not seem to be reliable with poor solutions. In some cases not over 60 per cent of the gold value was obtained.

See Appendix, page 188.

SECTION B.

Estimation of Gold Alone.

Any of the preceding methods are applicable if the silver be dissolved by parting with nitric acid in the usual way. The following methods serve, however, in cases where it is not necessary to estimate the silver.

Method No. 1.

Precipitation with Silver Nitrate.

This method, due to A. F. Crosse, is as follows: The solution is acidulated with nitric or sulphuric acid, and boiled to expel most of the hydrocyanic acid. Silver nitrate is then added as long as a precipitate forms, the solution allowed to settle, the clear liquid decanted through a filter, and the precipitate then collected on the same filter, dried, and the filter paper with residue wrapped in lead foil and cupelled. In some cases it is desirable to scorify before cupelling, or to fuse in a small crucible. For the latter purpose the following flux is recommended:

Glass, 110 parts.	Soda, 100 parts.
Litharge, 200 parts.	Argol, 48 parts.

The method gives fairly good results when the solutions are not too low in gold. The precipitate of silver cyanide carries down all but a small fraction of the gold, but with solutions very weak in gold the precipitation is not sufficiently perfect, as may be shown by evaporation of the filtrate with litharge.

Method No. 2.

Estimation of Gold by Reduction with Zinc after Adding Silver Nitrate.

The following description of a method proposed by Buchanan is given by M. Eissler ('The Cyanide Process'). The object of the preliminary addition of silver nitrate is by no means obvious.

"A known quantity of the solution is precipitated with excess of silver nitrate; the precipitate is decomposed by a reducing agent, filtered off, dried and cupelled. In practice the process was carried out as follows: 195 c.c. of the cyanide solution is transferred to a flask of 500 c.c. capacity, mixed with a few drops of potassium chromate. Silver nitrate of any strength (say 5 per cent) is then added until a reddish tinge of silver chromate remains permanent. Then take 10 to 20 grams of zinc dust or shavings, mix thoroughly with the precipitate and solution in the flask, add 2 to 3 c.c. of 10 per cent sulphuric acid. Allow to stand 10 minutes; add excess of sulphuric acid to dissolve the remainder of the zinc. Filter, wash once, dry

and incinerate on a roasting dish in muffle, and cupel residue with a little lead. The results are slightly lower than those obtained by the ordinary precipitation method."

Method No. 3.

Estimation of Gold by Direct Reduction with Zinc.

The following (H. T. Durant, *Journal* Chem. and Met. Soc. South Africa, Vol. III., p. 58) is stated to be a perfectly accurate and very rapid method of assaying gold-bearing solutions when large volumes of liquid have to be operated on.

"The solution for assay is placed in a boiling-flask of convenient size and rendered strongly acid with sulphuric acid, raised to the boiling point; about 5 grams of zinc shavings are then added in quantities of about 1 gram at a time, seeing that all action ceases from each addition of zinc before the next addition of zinc is made. The solution must be kept strongly acid throughout, adding more acid, if necessary, and must also be kept at boiling point through the whole operation. After the zinc has dissolved there will be a slight residue of lead, carbon, etc.; then remove from source of heat and add a few drops of lead acetate solution in order to form lead sulphate for collecting purposes, then filter through a double filter paper and wash out flask well on to the filter paper; then fold up the moist filter paper and place on a layer of borax in a scorifier to dry and char slowly in front of the muffle; when this is complete, add granulated lead or litharge and reducing agent and scorify as usual, cleaning the slag, if necessary. The method depends on the action of nascent hydrogen, and is by no means novel, at least in theory. If the zinc used is very pure and the acid therefore acts slowly, a few drops of copper sulphate solution may be added at the commencement to expedite matters."

See App., p. 189.

SECTION C.

Estimatiom of Silver Alone.

Method No. 1.

Precipitation as Sulphide and Cupellation.

A measured quantity of the solution, which must be alkaline, is mixed with an excess of sodium sulphide solution. When only small quantities of silver are present, it is better to add a few drops of lead

acetate or of the alkaline lead tartrate solution prepared by precipitating a soluble lead salt with tartaric acid, and, redissolving the precipitate in excess of caustic alkali. This forms a more bulky precipitate which carries down practically the whole of the silver. The precipitate generally settles rapidly and is easily filtered; when much zinc is present, however, there may be some difficulty, and in this case a little lime may be added.

After washing once or twice with dilute sodium sulphide solution, the filter containing the precipitate is dried, wrapped in lead foil and cupelled at a moderate temperature, or the paper may be allowed to burn slowly on a scorifier, and the ash mixed with grain lead, scorified and cupelled. The beads of silver obtained should be free from gold, and this will be the case if the sulphide precipitate has been sufficiently washed; but in any case it is better, after weighing, to dissolve them in dilute nitric acid and deduct the weight of any gold found.

Gold and copper are not precipitated from cyanide solutions by alkaline sulphides; in weak solutions the silver precipitate may carry down a little copper.

Method No. 2.

Volumetric Determination with Sodium Sulphide.

In cases where the cyanide solution contains no other metals except silver, precipitable by alkaline sulphides, a pretty fair approximation may be made by running in standard sodium sulphide to a measured volume of the liquid to be tested, until a drop taken out on a glass rod gives a brownish stain with a drop of an alkaline lead tartrate solution, or a purple color with sodium nitroprusside. The test may conveniently be made by placing the drops side by side on a strip of white filter paper, the reaction being clearly seen at the point where the two liquids meet.

The sodium sulphide may be accurately standardized by adding an excess of a solution of double cyanide of silver and potassium, filtering, and titrating the liberated cyanide in the filtrate in the ordinary way, after addition of potassium iodide.

$$1 \text{ gram KCy} \begin{cases} = 0.3 \text{ gram } Na_2S, \\ = 0.8284 \text{ gram Ag.} \end{cases}$$

Method No. 3.

Precipitation as Sulphide and Conversion into Bromide.

Allen (*Comm. Org. Anal.,* Vol. III., pt. 3) proceeds as follows: A definite measure of the liquid is boiled. Sulphuretted hydrogen is passed through or ammonium sulphide added. The silver is precipitated as Ag_2S, together with some copper and zinc, if these metals are present. The precipitate is washed, rinsed into a flask, and treated with excess of bromine water. If sulphur separates out, more bromine must be added, then boiling water. The silver bromide is then washed, dried, fused, and weighed as AgBr. AgBr $\times$ 0.57444 = Ag.

CLASS VII.

BASE METALS.

General Remarks. — The base metals which occur in ordinary cyanide solutions are present for the most part as double cyanides, consisting of more or less stable compounds of cyanogen with a heavy metal and one or other of the alkali or alkaline earth metals. Barium, calcium, etc., may be present as simple cyanides. In some cases (magnesium, aluminum, etc.) the metals may perhaps exist as hydrates, double chlorides, or other compounds not containing cyanogen.

The metals which most frequently require estimation in this connection are iron, zinc and copper.

The estimation of iron (as ferro- and ferricyanides) has already been described.

When metallic zinc in any form is used as a precipitant of gold or silver, some compound of zinc is necessarily introduced into the solution, and its estimation sometimes becomes a matter of importance.

We shall here discuss only the estimation of zinc and copper. The remaining metals are determined by the ordinary methods of analysis in the residue obtained by evaporation of the solution, after decomposing cyanogen compounds as described below. (Zinc, Method No. 1.)

SECTION A.

Estimation of Zinc.

Zinc is generally supposed to occur in cyanide solution as a double cyanide of the type of K_2ZnCy_4, though there is some evidence to show that this is partially dissociated in dilute solutions, which probably contain a portion of the zinc as the simple cyanide $ZnCy_2$. In certain cases potassium zincate $Zn(OK)_2$, or some similar compound, may be present.

Zinc may be determined as follows:

1. By the ordinary methods of analysis after decomposition of the cyanogen compounds.

2. By precipitation in acidulated solutions with ferrocyanide.

3. By precipitation in alkaline solutions with a soluble sulphide or with sulphuretted hydrogen.

4. By an alkalimetric method based on the reactions between zinc carbonate and ferrocyanide.

Method No. 1.

Estimation of Zinc after Decomposition of Cyanide by Evaporation with Acids.

In most cases the solution may be freed from all cyanogen compounds by adding to a measured volume (100 or 200 c.c.), say, 5 c.c. of concentrated nitric acid and 5 c.c. concentrated sulphuric acid, and evaporating, slowly at first, finally at a tolerably high temperature, until fumes of sulphuric anhydride (SO_3) are freely given off.

The residue should be free from carbonaceous matter, and should show no trace of any blue color on diluting and adding hydrochloric acid.

If this treatment fails to completely decompose the cyanogen compounds, it will be necessary to evaporate to complete dryness with nitro-hydrochloric acid, adding a little sulphuric acid. Evaporation with volatile acids alone would be liable to cause loss of zinc through volatilization of the chloride. In some cases a little potassium chlorate may be added with advantage.

After this treatment, add 2 or 3 c.c. of strong hydrochloric acid and dilute to about 15 or 20 c.c. Boil till all soluble matter is dissolved, then add excess of ammonia and boil again. Filter off any precipitate of ferric hydrate, silica, etc. If this is at all copious it will be necessary to redissolve the precipitate and again boil with excess of ammonia; filter again, adding the second filtrate to the first.

If copper is present, acidulate the filtrate with hydrochloric acid so as to have a slight excess of acid, and add some strips of lead; or acidulate with sulphuric acid and add sheet aluminum; in either case boil until the solution becomes colorless, filter, and determine zinc in the filtrate by any of the ordinary gravimetric or volumetric methods.

The separation of iron may also be made by precipitation as basic acetate in cases where the introduction of ammonium salts is to be avoided (as when zinc is afterwards to be precipitated as carbonate). This may be done as follows: After adding hydrochloric acid, neutralize with sodium hydrate or carbonate, and again acidulate very slightly with HCl. Boil, add sodium acetate in slight excess, boil again to precipitate iron and alumina as basic acetates. This precipitate must be washed several times by decantation with hot water before transferring to the filter, and, where very accurate determinations are required, must be redissolved and reprecipitated. The filtrate should be slightly acid, and perfectly clear and colorless.

Of the various gravimetric methods for estimating zinc, precipitation as carbonate and weighing as oxide is probably the best. (See Fresenius, *Quant. Anal.*, 7th ed., Vol. I., pp. 197, 433.) Great care is necessary to wash the precipitate thoroughly, and, in igniting, to avoid reduction of the oxide to metallic zinc,

$$ZnO \times 0.8042 = Zn.$$

The volumetric methods in general use are based on one of two principles: (*a*) Precipitation as ferrocyanide; (*b*) Precipitation as sulphide.

(For details see Sutton, *Volum. Anal.*, 8th ed.)

Method No. 2.

Estimation of Zinc by Precipitation as Ferrocyanide in Acid Solution.

In cases where the solution originally contained no ferrocyanide, thiocyanate, or other substance capable of reducing permanganate, and where metals other than zinc which could be precipitated by ferrocyanide in presence of free sulphuric acid and hydrocyanic acid are also absent, it is possible to estimate the zinc as follows (*Proceedings* Chem. and Met. Soc. South Africa, Vol. I., p. 207):

A solution of potassium ferrocyanide is accurately standardized with reference to a solution of potassium permanganate, in the manner described under 'Reducing Agents.' A measured volume of the liquid to be tested is mixed with a definite volume of the standard ferrocyanide solution, diluted to about 200 c.c., or until not more than 0.1 gram ferrocyanide is present per 100 c.c. of the liquid. It is then acidified quite strongly with sulphuric acid and

titrated with permanganate. The equivalent of the amount of permanganate used is then deducted from the amount of ferrocyanide added, the difference being the amount of ferrocyanide used in precipitating zinc.

As the precipitated ferrocyanide of zinc interferes with the titration with permanganate, the excess of ferrocyanide must be determined by making up the solution to a definite volume, allowing to settle, and titrating a measured quantity of the clear liquid. The addition of a little pure powdered chalk, before acidulating strongly with sulphuric acid, was found to promote the settlement of the zinc ferrocyanide. The ferrocyanide should be standardized by means of a zinc cyanide solution containing a known amount of zinc.

Method No. 2 (modified).

A. F. Crosse (*Journal* Chem. and Met. Soc. South Africa, Vol. III., p. 5, May 10, 1902) describes the following modification of the above process, for cases in which ferrocyanides, etc., are present in the original solution.

The ferrocyanide is determined by Bettel's method before and after the precipitation of the zinc, the difference of the two titrations representing the ferrocyanide converted into a ferrocyanide of zinc and precipitated.

Crosse gives the following equation:

$$K_4FeCy_6 + 2K_2ZnCy_4 + 4H_2SO_4 = Zn_2FeCy_6 + 4K_2SO_4 + 8HCy,$$

or 1 part $K_4FeCy_6 = 0.353$ part of zinc.

A. Whitby (*Journal* Chem. and Met. Soc. South Africa, Vol. III., p. 15, June 21, 1902) states, however, that potassic zinc ferrocyanide is generally believed to be formed, the reaction consequently taking this form:

$$2K_4FeCy_6 + 3K_2ZnCy_4 + 6H_2SO_4 = K_2Zn_3(FeCy_6)_2 + 6K_2SO_4 + 12HCy,$$

which materially alters the calculation, since, if the latter equation be correct,

$$1 \text{ part } K_4FeCy_6 = 0.265 \text{ part of zinc.}$$

It is necessary to add about 0.1 per cent of ferrocyanide of potassium to the cyanide solution.

The method is carried out as follows:

(*a*) 20 c.c. N/100 $KMnO_4$ is placed in an evaporating dish with

some dilute sulphuric acid, and the cyanide is run in from a burette till the color disappears. The result is calculated into the equivalent of K_4FeCy_6. Let A = K_4FeCy_6 used per 100 c.c. of cyanide solution.

(*b*) A second portion of the solution is taken and mixed with an equal volume of dilute sulphuric acid (5 per cent by volume) and the ferrocyanide of zinc filtered off. The clear solution is then taken, poured into a burette, and run into 10 c.c. of N/100 $KMnO_4$ and the result calculated into its equivalent in K_4FeCy_6. Let B = K_4FeCy_6 per 100 c.c. of the original cyanide solution. A — B is equivalent to the amount of ferrocyanide precipitated by the zinc.

1 c.c. N/100 $KMnO_4$ = 0.0036831 gram K_4FeCy_6.

Thiocyanates and other substances which reduce permanganate in acid solution do not interfere, as they remain the same in both determinations.

Of course this method is only applicable for solutions containing chiefly zinc, and with mere traces of copper, etc. Before titrating it is advisable to warm the solution slightly.

Instead of using permanganate, it is probable that the excess of ferrocyanide might be determined by titration with standard copper sulphate solution, using a ferric salt as external indicator as in Bohlig's method for ferrocyanides (see above).

Method No. 3.

Estimation of Zinc by Direct Precipitation as Sulphide.

Other metals precipitable from a cyanide solution by alkaline sulphides (*e.g.*, silver and mercury) must be absent.

A sodium sulphide solution is prepared by dividing a caustic soda solution into two equal portions, saturating one part with sulphuretted hydrogen, then mixing with the other portion. The solution may be standardized against a zinc sulphate solution containing, say, 43.82 grams $ZnSO_4 \cdot 7H_2O$ per liter, in which case 1 c.c. = 0.01 gram Zn, and adjusted until it corresponds volume for volume with the zinc solution.

When zinc is precipitated by direct addition of an alkaline sulphide to a cyanide solution, the precipitation is never quite complete, as zinc sulphide is not absolutely insoluble in alkaline sulphides. In all cases the precipitation is better in a warm solution,

and in some cases it appears to be necessary to make the liquid strongly alkaline with caustic soda.

The finishing point may be found by various external indicators, among which may be mentioned:

(*a*) Alkaline lead tartrate. (*c*) Chloride of nickel.
(*b*) Sodium nitroprusside. (*d*) Metallic silver.

Or a small quantity of a ferric salt may be added, which forms red flakes of ferric hydrate in the alkaline liquid. On running in the sodium sulphide from a burette, a white precipitate of zinc sulphide is formed at first, but when the zinc is completely precipitated, any excess of sodium sulphide causes a blackening of the flakes of ferric hydrate, which thus acts as an internal indicator.

The lead tartrate indicator is prepared by mixing tartaric acid and caustic soda, then adding lead acetate till a permanent precipitate forms, then excess of soda until the precipitate redissolves. The slightest excess of sulphide is shown by placing drops of the liquid and of the indicator side by side on white filter paper, when a dark stain is produced where the two liquids meet.

A bright silver disc may also be used for determining the end point; a drop of the liquid is taken out on a glass rod and placed for 10 or 20 seconds on the silver surface. Zinc sulphide itself has no effect on the silver, but any excess of alkaline sulphide tarnishes the silver at once.

Method No. 4.

Estimation of Zinc by Precipitation as Sulphide, and Determining Excess of Sulphide.

It seems to be pretty generally agreed that the direct determination of the end-point in the previous method is uncertain and indefinite, at least in ordinary working cyanide solutions. Hence several methods have been suggested for determining the excess of sulphide, after adding a known amount of standard solution more than sufficient for complete precipitation of the zinc.

The following will be here noticed:

(*a*) Excess of sulphide determined by sodium nitroprusside as in Dr. Loevy's method.

(*b*) Excess of sulphide determined by double cyanide of silver and potassium.

Method No. 4 (*a*).

Excess of Sulphide Determined by Sodium Nitroprusside.

After precipitating the warm solution with sodium sulphide the liquid is filtered and the precipitate washed free from sulphide. The filtrate is then titrated by the colorimetric method described above. (See Sulphides.)

Method No. 4 (*b*).

Excess of Sulphide Determined by Double Cyanide of Silver and Potassium.

This process has been described by the writer (*Chemical News*, March 13, 1903). It depends upon the fact that sulphides decompose the double cyanide of silver and potassium, with liberation of an equivalent amount of cyanide, thus:

$$2KAgCy_2 + K_2S = Ag_2S + 4KCy.$$

(*a*) After precipitating the zinc (best in a warm, strongly alkaline solution) with sodium sulphide, the liquid is filtered while still hot, and washed thoroughly till the precipitate is free from soluble sulphides. Another method is to cool to the temperature of the room, make up to a definite volume (say, 200 c.c.), and filter off an aliquot part (say, 100 c.c.).

In either case the filtrate is mixed with a moderate excess of a double cyanide solution [prepared by adding silver nitrate to a solution of pure cyanide (say, 0.5 per cent KCy) until a permanent precipitate forms, allowing to stand and filtering].

After thorough agitation with this liquid the precipitate of silver sulphide is allowed to settle, filtered and washed. 5 c.c. of 1 per cent potassium iodide is added to the filtrate, which is then titrated in the ordinary way with standard silver nitrate solution.

The result gives the cyanide originally present, together with that liberated by the excess of sulphide.

(*b*) Another portion of the liquid is titrated direct with silver nitrate, using the alkaline iodide indicator to determine total cyanide. This result deducted from the first gives the equivalent of the excess of sulphide.

The sodium sulphide solution is standardized also by means of the double silver cyanide solution,

$$1 \text{ gram KCN} = \begin{cases} 0.3 \text{ gram } Na_2S. \\ 0.25 \text{ gram Zn (more exactly, 0.2523).} \end{cases}$$

Method No. 5.

Precipitation of Zinc as Sulphide, and Determination by Decomposing the Precipitate with an Oxidizing Agent.

Two processes based on this principle are described by A. F. Crosse, in which the sulphide of zinc is decomposed: (*i*) by ferric sulphate; (*ii*) by iodine.

Method No. 5 (*a*).

Zinc Sulphide Decomposed by Ferric Sulphate.

The following method (*Journal* Chem. and Met. Soc. South Africa, Vol. III., p. 4, May 10, 1902) for solutions containing not more than a trace of copper is stated to be very exact and fairly quick:

"Take 300 c.c. of solution, add about a gram of KCy and the same quantity of pure caustic potash or soda, heat nearly to boiling point, and then add a slight excess of sulphide of sodium in solution. The zinc will be quickly precipitated as sulphide, and should be collected on a filter paper and washed with hot water. Then place the filter paper in a wide-mouthed bottle of known capacity, between 250 and 300 c.c. This bottle must be provided with a well-fitting india-rubber bung through which a moderately wide tube is inserted, about 8 or 10 in. long. Then fill up the bottle with a weak solution of pure ferric sulphate, containing 5 per cent to 7 per cent of sulphuric acid, place the bottle or flask in a bowl of cold water and raise the temperature to boiling point. The reason for the glass tube will be apparent, as it allows for the expansion of the liquid.

"The zinc sulphide will have decomposed [$ZnS + Fe_2(SO_4)_3 = 2FeSO_4 + ZnSO_4 + S$], and reduced a proportionate amount of ferric sulphate to ferrous sulphate.

"When nearly cold, filter off the solution through a dry filter paper, take half the quantity contained in the bottle and titrate with N/10 permanganate: 1 c.c. N/10 $KMnO_4$ = 0.003285 gram Zn."

The results in presence of ferro and sulphocyanides were found by Crosse to be very satisfactory.

Owing to the slight solubility of zinc sulphide in weak cyanide solutions, an addition of one milligram of zinc per 100 c.c. of solution taken should be made as a correction to the result obtained.

Method No. 5 (*b*).

Zinc Sulphide Decomposed by Iodine.

The following method described by Crosse (*Journal* Chem. and Met. Soc. South Africa, Vol. III., p. 165) is quoted from Mohr's *Volumetric Analysis,* p. 338.

The solutions required are:

(*a*) N/10 iodine.

(*b*) N/10 thiosulphate.

(*c*) 5 per cent sodium sulphide.

The method is as follows: 100 c.c. of the working solution is heated to about 70° C., and an excess of sodium sulphide added. The mixture is allowed to settle, filtered, and the precipitate of zinc sulphide well washed on the filter with hot water; the washing is continued until the wash-water shows no trace of sulphide; the filter paper is then transferred to a small 150 c.c. flask. This flask is fitted with a rubber cork having two holes; through one passes a drip funnel with tap, and through the other a short piece of glass tube, terminating in a small length of rubber tubing. A pinch-cock is attached to the latter. Sufficient N/10 iodine is then run into the flask to leave an excess of not more than 5 c.c. (30 to 35 c.c. N/10 iodine is usually sufficient). The cork is then replaced, and about 100 c.c. of very dilute hydrochloric acid is placed in the funnel. The tap is opened, and on pressing the pinch-cock air escapes and the dilute acid takes its place. The taps are then closed, and the whole apparatus shaken to thoroughly break up the filter paper. After a few minutes' standing the contents of the flask are titrated with N/10 thiosulphate, and the excess of iodine determined.

If x = No. of c.c. N/10 iodine taken,

y = No. of c.c. N/10 thiosulphate required,

$(x - y) \times 0.003285$ = grams Zn per cent.

The reactions are as under:

$$ZnS + 2HCl = ZnCl_2 + H_2S.$$
$$H_2S + I_2 = 2HI + S.$$

The method is rapid of execution and capable of great accuracy.

Method No. 6.

Estimation of Zinc by Alkalimetric Method, Based on Precipitation as Carbonate and Treatment with Potassium Ferrocyanide.

This method, due to L. M. Green (*Proceedings* Inst. Min. and Met., Vol. X., pp. 29-37), depends on the fact that when an excess of ferrocyanide is mixed with a precipitate of basic carbonate of zinc, there is a liberation of alkali in proportion to the zinc present. It is carried out as follows:

(*a*) 50 c.c. of the solution to be tested are examined for total cyanide by Vielhaber's method (see above), to determine the amount of standard silver nitrate required to give a permanent red tinge when a drop of neutral potassium chromate has been added. If necessary, the protective alkali must be neutralized by adding the required amount of N/10 nitric acid before titrating with $AgNO_3$ and chromate.

Let n = No. of c.c. of $AgNO_3$ required.

(*b*) Another 50 c.c. of the original solution are now taken, n c.c. of silver nitrate added, and well shaken. A few drops of phenol phthaleïn solution (0.5 per cent in alcohol) are now added, and then N/10 sodium carbonate, until a distinct pink tinge is permanent. The solution is now very cautiously neutralized by the addition of N/10 nitric acid until the color is just discharged. The liquid should be allowed to stand for a few moments after each addition of acid, and the color of the clear liquid observed in a good light against a white background, as the precipitate may remain slightly tinged after the liquid is really neutral. According to Green, the zinc is thus precipitated as basic carbonate. An excess of ferrocyanide is now added, which liberates alkali in proportion to the amount of zinc present. This alkali is now determined by titrating the resulting pink fluid with N/10 nitric acid, until it again becomes colorless or faintly yellow.

The reactions, so far as the zinc double cyanide is concerned, appear to be as follows, according to the explanations given in Green's paper:

(*a*) On adding silver nitrate we get in succession

$$K_2ZnCy_4 + AgNO_3 = ZnCy_2 + KAgCy_2 + KNO_3,$$
$$KAgCy_2 + AgNO_3 = 2AgCy + KNO_3,$$
$$ZnCy_2 + 2AgNO_3 = Zn(NO_3)_2 + 2AgCy.$$

Or, combining these in one equation:

$$K_2ZnCy_4 + 4AgNO_3 = 4AgCy + Zn(NO_3)_2 + 2KNO_3.$$

(*b*) On adding sodium carbonate to neutralize

$$2Zn(NO_3)_2 + 3Na_2CO_3 + 2H_2O =$$
$$Zn(OH)_2{\cdot}ZnCO_3 + 2NaHCO_3 + 4NaNO_3.$$

[The experimental results I have obtained do not confirm this equation, but point rather to a reaction in equivalent proportions between zinc and sodium carbonate, in which case the precipitate would appear to consist of the normal carbonate, thus:

$$Zn(NO_3)_2 + Na_2CO_3 = ZnCO_3 + 2NaNO_3.$$

The matter, however, requires further investigation.]

(*c*) On adding ferrocyanide, alkali is liberated

$$Zn(OH)_2{\cdot}ZnCO_3 + K_4FeCy_6 = Zn_2FeCy_6 + 2KOH + K_2CO_3$$

[Or in case of normal zinc carbonate

$$2ZnCO_3 + K_4FeCy_6 = Zn_2FeCy_6 + 2K_2CO_3.]$$

(*d*) On titration with standard nitric acid (phenol phthaleïn indicator),

$$2KOH + K_2CO_3 + 3HNO_3 = 3KNO_3 + KHCO_3 + 2H_2O, \text{ or}$$
$$2K_2CO_3 + 2HNO_3 = 2KHCO_3 + 2KNO_3.$$

This method was found to give fair comparative results for varying quantities of zinc. It requires the use of considerable amounts of silver solution, however, and the neutralization with sodium carbonate and N/10 acid is somewhat tedious, the finishing point being rather indefinite. (See Appendix, pages 196, 197.)

SECTION B.

Estimation of Copper.

The presence of copper in the ore under treatment, especially when the metal occurs as carbonate, has a very injurious effect, giving rise to high consumption of cyanide. Moreover, the accumulation of copper in the working solutions beyond a certain amount interferes seriously with the precipitation of the gold. Hence in some

cases it becomes a matter of importance to estimate the quantity of copper in the solution.

Detection of Copper.—The presence of copper, even in very small amount, may be detected by acidulating the cyanide solution with any mineral acid, and adding a few drops of dilute ferrocyanide solution, which gives the characteristic reddish-brown color.

Ammonia, of course, gives no blue color in solutions containing soluble cyanides, so that complete decomposition (*e.g.*, by boiling with sulphuric and nitric acids) is necessary before this reagent can be applied for the detection of copper.

Methods for Estimating Copper.—The following are here given:—

(*a*) Decomposition of the solution by evaporation with acids, copper being afterwards estimated by the ordinary analytical methods.

(*b*) By direct precipitation from cyanide solution as cuprous cyanide, by addition of acid.

Group (a).—Decomposition of Solution by Boiling or Evaporation with Acids.

Method No. 1.

Evaporation with Nitro-Hydrochloric Acid, Followed by Sulphuric Acid.

This process has already been described under zinc. (See above, Method No. 1.) In the majority of cases it appears to be unnecessary to evaporate to complete dryness; it is sufficient to add to 100 c.c. of the solution 5 c.c. of concentrated nitric and 5 c.c. of concentrated sulphuric acid and boil till white fumes of SO_3 are freely given off, then add ammonia in slight excess, boil again and filter. If much iron is present, redissolve the precipitate in hydrochloric acid and reprecipitate with ammonia, filter again, adding the second filtrate to the first.

The copper may now, of course, be estimated by any of the ordinary gravimetric or volumetric methods, of which the best known are the 'cyanide' method of Parkes and the 'iodide' method of E. O. Brown, both of which are extensively used with various modifications, and are described in all text-books on analysis. For rapid

estimations, however, the simplest plan is to use a colorimetric method. For this purpose a standard solution of copper nitrate is prepared, containing 0.1 per cent copper and about 1 per cent sulphuric acid. The ammoniacal copper solution from the cyanide liquor, diluted to a suitable volume, (according to the amount of copper present) say 10 c.c., for every milligram of Cu, is placed in a clear glass cylinder, and a nearly equal volume of distilled water in a similar cylinder. To the latter add as nearly as possible the same amount of ammonia as was used in the test, and run in the copper solution from the burette, with constant shaking, until the tint in the two cylinders is the same. Every c.c. run in represents 0.001 gram Cu. The best results are obtained when the amount of copper is between 5 and 15 milligrams. With practice, the amount of copper present may be estimated to within 0.0002 gram. Some difficulty is occasionally experienced in getting the same kind of color in the two liquids; this appears to be chiefly owing to a trace of iron passing with the filtrate into the ammoniacal liquor, to which it imparts a greenish shade; when this occurs, no accurate comparison of the tints is possible. (See Appendix, page 198.)

Where the quantity of copper present is sufficient, it may be estimated quite accurately in the liquid obtained by boiling with sulphuric acid till fumes are given off, by diluting this liquid carefully to about 100 c.c., adding 10 c.c. of concentrated sulphuric acid, and one or more sheets of aluminum, boiling for 10 minutes and treating the precipitated copper by the method of A. H. Low (*Journal* Amer. Chem. Soc., XVIII., No. 5; see also Sutton, *Volum. Anal.*, 8th ed., p. 203).

Method No. 2.

Treatment with Silver Nitrate and Digestion with Acid.

This process is a slight modification of the method of H. Rose for determining total cyanide which has been already described.

(*a*) A determination is made of the amount of silver nitrate required for total precipitation of cyanides and chlorides with chromate indicator. (See Vielhaber's method, above.)

(*b*) Another portion of the original liquid is now taken (say, 10 to 50 c.c.), and the amount of silver nitrate shown to be necessary by the previous test for complete precipitation of cyanides, ferrocyanides, chlorides, etc., is added with agitation, then 5 c.c. of

concentrated sulphuric acid. The mixture is then boiled till the residue in the flask is perfectly white, or has only a slight brownish tinge, then filtered, and the flask and filter washed once or twice with a little hot water, keeping the bulk of liquid as small as possible. All the copper will now be in solution as sulphate, and may be estimated as in the previous method.

Group (b).—Precipitation of Copper in Cyanide Solution by Direct Addition of Acid.

When sulphuric acid is added in slight excess to a solution containing a soluble double cyanide of copper, a white precipitate, probably cuprous cyanide (Cu_2Cy_2), is formed, and the greater part of the copper is thrown down. It is always possible, however, to detect copper in the filtrate by the ferrocyanide test.

The following method devised by the present writer (*Journal* Soc. Chem. Ind., Vol. XIX., p. 14) gives accurate results under certain conditions, but is not applicable in the presence of zinc, silver or ferrocyanides.

It depends upon the facts:

1. That cuprous cyanide is precipitated from a solution of the double cyanide by dilute mineral acids.

2. That hydrocyanic and carbonic acids have practically no action on methyl orange.

3. That when an acid is added gradually to a mixed solution containing free cyanide, alkaline hydrates and carbonates, and a double cyanide of copper, no precipitation of copper occurs until the whole of the cyanides and alkaline compounds have been neutralized to methyl orange.

The test is made by adding N/10 acid in slight excess to a measured volume of the liquid, making up to a definite volume, filtering, and titrating an aliquot part of the filtrate with N/10 sodium carbonate, using methyl orange as indicator.

The initial point of precipitation with N/10 acid must be carefully noted, *i.e.*, the point at which the liquid first remains permanently turbid owing to precipitation of cuprous cyanide. From the total amount of acid added beyond this initial point, the equivalent, for the entire filtrate, of the amount of N/10 carbonate used must be deducted. The result gives the amount of N/10 acid consumed in precipitating copper. The reaction is apparently

$$K_2Cu_2Cy_4 + 2HNO_3 = 2KNO_3 + 2HCy + Cu_2Cy_2.$$

With impure solutions a difficulty is sometimes experienced in observing the initial point; also the titration with methyl orange does not give as sharp an end point as could be wished.

SECTIONS C, D, E.

Estimation of Iron, Alkaline Earths and Alkali Metals.

See Appendix, pages 195, 196.

CLASS VIII.

SUSPENDED MATTER.

General Remarks.—The nature and amount of the solid matter in suspension may be of considerable importance under certain conditions. It is well known that imperfect precipitation is often caused by turbid solutions, and in some cases much trouble is caused by deposits of various kinds forming on the surface of the zinc shavings, etc. It is advisable to ascertain by occasional tests whether the amount of suspended matter in the solution is increasing or not. The insoluble substances carried down from the leaching tanks may be very various in character, but among those most commonly found may be mentioned: (1) Finely divided silica; (2) cyanides and ferrocyanides of zinc; (3) ferric hydrate, alumina and magnesia; (4) calcium carbonate; (5) organic matter resulting from decaying vegetation mixed with tailings.

In some cases the suspended matter may be reduced in amount or entirely dissolved by increasing the cyanide strength or the alkalinity of the solution, as, for example, when sparingly soluble zinc compounds are present.

As a general rule it will be sufficient to determine the total amount of suspended matter, but occasionally an analysis of the dried residue may be required.

We shall also give a method of estimating total dissolved solids.

SECTION A.

Estimation of Total Solids in Suspension.

For this purpose a measured volume (say 500 c.c. or 1,000 c.c.) of the solution is passed through a weighed filter paper, and the paper weighed again after washing and drying. When an accurate determination is required it is carried out as follows:

(*a*) *Preparation of Filters.*—About a dozen filter papers of good quality and as free as possible from ash are taken. These may conveniently be about 9 c.m. in diameter. The filters, several together,

are folded one within the other in funnels, and washed with hot dilute hydrochloric acid until the washings show no trace of iron or other soluble matter. They are then washed with hot distilled water until no trace of chlorine can be detected in the liquid passing through, on testing it with silver nitrate. The papers are then spread out and dried thoroughly on a water bath.

(*b*) *Determination of Ash.*—Six of the prepared papers may be taken for this purpose. They are folded together into a small packet and wrapped round once or twice with one end of a piece of platinum wire. Holding the wire by the other end, the papers are held in a small gas flame, in a place free from draughts, until completely burned. The ash is allowed to fall into a clean porcelain crucible, which has previously been ignited and weighed; this is then again ignited with the ash, allowed to cool, and weighed. The quantity of ash found, divided by 6, gives the average weight of ash for one paper.

(*c*) *Weighing of Paper for Collection of Suspended Matter.*—The paper to be used for this purpose is dried for some time on the water bath, placed in a weighing tube and weighed. The weighing tube may easily be made from a couple of test tubes, one of which fits tolerably closely within the other. The rim of the smaller tube is cut off, and the edges melted smooth in a small gas flame. When the paper is to be weighed it is carefully rolled up and slipped inside the smaller tube, the larger tube being then put on as a cover. After weighing, the paper is returned to the water bath and weighed again at intervals of half an hour until the weight is nearly or quite constant. Two consecutive weighings should agree at least within 0.5 milligram. The weight of the empty tubes is then deducted. The tubes and paper should be placed in a desiccator to cool before weighing.

The tubes, during drying, may conveniently be supported over the water bath on a sheet of paper folded in grooves. The filter is placed almost out of the smaller tube, the two tubes being separated; they can then be shut up while hot by pushing the tubes together on the grooved paper.

Filtration will generally be more rapid if the paper be folded to form a ribbed filter before drying.

(*d*) *Filtration of Suspended Matter.*—When the quantity of suspended matter is very large, it will be better to allow a sample of the liquid to remain at rest for several hours and siphon off the

clear liquor, which may then be passed through the filter, and the sediment added after the whole of this has filtered through. In other cases, where the amount of sediment is not excessive, the measured quantity may be placed in a narrow-necked flask and inverted over the funnel containing the weighed filter paper. Finally, the residue adhering to the sides of the flask is carefully rinsed out on to the funnel with hot distilled water, and the filter washed until the washings show no indications of soluble matter.

(*e*) *Drying and Weighing of Suspended Matter.*—The washed filter, with the matter upon it, is now dried on the water bath with the weighing tubes exactly as before. The weight found, less weight of tubes and paper alone (determined above, under *c*), gives the total solids in suspension, dried at 100° C.

SECTION B.

Estimation of Various Constituents in Suspended Matter.

The paper with its contents, after drying and weighing as above, is ignited in a porcelain crucible, allowed to cool and weighed. The amount found, less ash of prepared filter paper, gives the weight of mineral matter in suspension.

The loss of weight on ignition represents volatile matter, consisting of organic matter, carbonic acid, combined water, etc.

Examination of Ignited Residue.—The contents of the crucible may be transferred to a small porcelain dish and digested for some time with concentrated hydrochloric acid, on a sand bath, finally evaporating to complete dryness and igniting gently. The residue is then examined by the ordinary methods of analysis for silica, zinc, iron, copper, calcium, magnesium, alkalis, etc.

It is perhaps advisable to determine zinc, and some other metals which might volatilize either on ignition or on treatment with concentrated hydrochloric acid, in a separate portion of the residue, dried on the water bath without ignition. For this purpose the residue is digested with nitro-hydrochloric acid, then concentrated to a small bulk, a few drops of sulphuric acid added, and evaporation continued until SO_3 is given off. Zinc, iron, copper, etc., will then be present as sulphates.

Determination of Calcium and Magnesium.—After separation of silica, copper, zinc, iron, aluminum, etc., by treatment with acids, H_2S, ammonia and ammonium sulphide, in the ordinary way, the filtrate is evaporated with nitric acid until all excess of sulphide is oxidized, filtering again if necessary. Hydrochloric acid is then added, heated to boiling, then ammonia in excess, finally oxalic acid in quantity sufficient to precipitate the calcium, leaving an excess of ammonia. The liquid is well stirred and allowed to stand until it has settled clear, filtered, washed with hot water till free from chlorides, and the precipitate strongly ignited and weighed as CaO.

The filtrate from the calcium oxalate precipitate is evaporated to a small bulk, a few drops of ammonia added, then sodium phosphate, stirred without touching the sides of the beaker with the rod, allowed to settle, filtered, and the precipitate washed on to the filter paper with a little of the filtrate; finally washed with 25 per cent ammonia till free from chlorides, ignited, and weighed as magnesium pyrophosphate, $Mg_2P_2O_7$.

SECTION C.

Estimation of Total Solids in Solution.

A portion of the filtrate from the suspended matter, taken before washing the latter with hot water, may be used for estimating total solids in solution.

Carefully clean and ignite a small porcelain basin, noting its exact weight when cool. The basin must be of such a size that it may be conveniently placed on the pan of an analytical balance, and in a desiccator. Evaporate 100 or 200 c.c. of the solution to dryness in this basin, on water bath; when the residue appears quite dry, wipe the under side of the basin with a cloth, and transfer to desiccator till cool. Weigh approximately, place again on water bath. Weigh again at intervals of half an hour. Before removing the dish from the desiccator it is advisable to place the weights previously required on the balance pan, so as to be able to take the actual weight of dish and contents as rapidly as possible. The dried residue usually absorbs moisture and increases in weight on the balance very rapidly. Repeat the operation till the difference in

weight between two successive weighings is less than 1 milligram. About three hours are generally required, after the residue is apparently dry, before the weight is constant.

Weight of dish and contents, less weight of empty dish, gives total solids in solution, dried at 100° C.

Note color and appearance of residue.

Total Solids on Ignition.—In some cases it is useful to heat the basin and contents gradually to redness, after having obtained a constant weight on the water bath. The further loss of weight on ignition gives an idea of the amount of volatile matter—cyanogen, CO_2 in carbonates, organic matter of various kinds, ammonium salts, water of crystallization, etc. Note especially if any charring takes place, if fumes are evolved, or if there are any changes of color. Allow to cool in desiccator, weigh, ignite again, cool, and weigh till weight is constant.

The residue may now be used for determination of silica, iron, aluminum, calcium, magnesium, potassium, sodium or other metals.

AN EXAMINATION OF VARIOUS METHODS FOR THE ESTIMATION OF FERROCYANIDES.

The following investigation was undertaken with a view to ascertaining which of the numerous published processes for the estimation of ferrocyanides would be most suitable for use in dealing with the solutions obtained in the cyanide treatment of ores. None of the methods examined proved to be entirely satisfactory, though in some cases a slight modification naturally suggested itself, which gave decidedly better results than the original form of the process. The following is a short summary of methods examined, which were selected as being the most promising:

Summary of Methods Examined.

(1) *Titration of iron,* after decomposition of the cyanogen compounds with acids.

(*a*) Without precipitating the iron as hydrate.

(*b*) By precipitating with ammonia and determining iron in the precipitate.

(2) *Inverse titration with permanganate.*

(*a*) Running solution to be examined into a measured volume of standard permanganate (Bettel's method).

(*b*) Determining excess of permanganate by means of potassium iodide and thiosulphate.

(3) *Precipitation as Prussian blue,* treating precipitate with alkali, filtering and titrating the acidulated filtrate.

(*a*) With permanganate (Erlenmeyer's method).

(*b*) With copper sulphate (Knublauch's method).

(4) *Direct titration with standard copper sulphate* and ferric indicator (Bohlig's method).

(5) *Conversion into ferricyanide and titration* of the latter with copper sulphate and ferrous indicator.

(*a*) Converted by bleaching powder (Hurter's method).

(*b*) Converted by permanganate.

(6) *Titration with standard zinc sulphate* (Müller's method).

(7) *Green's alkalimetric method.*

Method No. 1.

Titration of Iron.

This method is based on the assumption that all the iron in the solution is present as ferrocyanide. As generally carried out, the solution is evaporated several times to dryness with strong acids, in order to ensure the complete decomposition of the cyanogen compounds. In most cases, however, this was found to be unnecessary, and complete removal of cyanogen could be effected as follows:

Method No. 1 (*a*). *Without Precipitation of Iron as Hydrate.*— A measured volume of a solution containing the usual impurities found in cyanide liquors (K_2ZnCy_4, KCyS), together with a known volume of N/100 ferrocyanide (4.22 grams $K_4FeCy_6 \cdot 3H_2O$ per liter), was evaporated with addition of 5 c.c. concentrated nitric acid and 10 c.c. sulphuric acid (25 per cent per volume of strong acid), until dense white fumes of sulphuric acid were evolved. When cool, 25 c.c. water and 10 c.c. of the above 25 per cent sulphuric acid were added, then one gram of clean zinc, and the mixture heated gently until the zinc had completely dissolved. The flask was then cooled, 50 c.c. of boiled distilled water added, and the solution titrated immediately with N/100 permanganate.

The sulphuric acid used was prepared by dropping permanganate solution into the diluted acid, after cooling, until a very faint pink tint remained permanent.

The zinc used left a small quantity of black residue on dissolving in acid. It was not found advisable to filter this off, but a correction was made by carrying out a blank experiment, using the same weight of zinc and of other ingredients, but omitting ferrocyanides. The amount of permanganate finally required in titrating the blank test was deducted from the numbers obtained in the other determinations. Usually, however, it was found that a larger correction than that shown by the blank test was necessary, in order to give numbers approximately proportional to the ferrocyanide taken.

For convenience in comparison the results of each determination have been calculated so as to show the percentage variation from the mean result. (See last column.)

Table No. 1. *Results of Method No.* 1 (*a*).

Model Solution A used in tests.

KCy	0.192%,
K_2ZnCy_4	0.076%,
KCyS	0.03 %.

Permanganate (standard solution)

1 c.c. = 0.000536 gram Fe.
= 0.04042 gram $K_4FeCy_6 \cdot 3H_2O$.

Solutions Tested.		(*a*) Standard permanganate required.	(*b*) Corrected volume of permanganate. b = a — 4.1	(*c*) Permanganate per 100 c.c. of N/100 ferrocyanide.	(*d*) Percentage results. 94.3 = 100
N/100 Ferrocyanide c.c.	Solution A taken. c.c.	c.c.	c.c.	c.c.	
10	50	13.45	9.35	93.5	99.2
20	50	22.7	18.6	93.	98.6
25	50	28.25	24.15	96.6	102.4
30	50	32.25	28.15	93.8	99.5
40	50	42.25	38.15	95.4	101.2
50	50	50.9	46.8	93.6	99.3

The results obtained in a similar series of tests with pure ferrocyanide (without adding KCy, K_2ZnCy_4 and KCyS) showed about the same degree of divergence. We may conclude, therefore, that this method, with the proper corrections, would give results within about ± 2.5 per cent of the actual amount of ferrocyanide present.

Method No. 1 (*b*). *Precipitating Iron with Ammonia.*—A measured volume of the solution to be tested, containing a known amount of ferrocyanide, was evaporated with 5 c.c. concentrated nitric acid and 10 c.c. special 25 per cent sulphuric acid—prepared as described under Method No. 1 (a)—until white fumes were freely evolved, and the cyanogen compounds appeared to be completely decomposed. After cooling somewhat, 5 c.c. of concentrated hydrochloric acid were added, heated to boiling, then 25 c.c. of water, and ammonia in slight excess. After again boiling, the precipitate of ferric hydrate was filtered off and washed with hot water till free from chlorides. It was then dissolved from the filter paper into a clean flask by means of 10 c.c. of special sulphuric acid, the paper washed with hot water till free from iron, collecting the washings in the same flask, and reduced by dissolving 1 gram of clean zinc in the liquid. When the zinc had completely dissolved, the flask was cooled, 50 c.c. of boiled distilled water added, and the solution titrated immediately with permanganate.

As in the previous method, a correction is necessary, as not only the zinc, but also the filter papers contain a small amount of iron or other reducing agent. A blank experiment is conducted exactly as in the actual determinations, but omitting ferrocyanide.

This method has the advantage that zinc, copper, etc., may be determined in the filtrate from the ferric hydrate precipitate.

Table No. 2. Results of Method No. 1 (b).

Model Solution A { KCy 0.192%, K_2ZnCy_4 0.076%, KCyS 0.03%.

Standard Permanganate { 1 c.c. = 0.000536 gram Fe, = 0.04042 gram $K_4FeCy_6 \cdot 3H_2O$.

Solutions Tested.		(a) Standard permanganate required.	(b) Corrected volume of permanganate. b = a — 1.5	(c) Permanganate per 100 c.c. of N/100 ferrocyanide.	(d) Percentage results. 104 = 100
N/100 Ferrocyanide taken. c.c.	Solution A taken. c.c.	c.c.		c.c.	
10	50	11.9	10.4	104	100
20	50	22.6	21.1	105.5	101.4
25	50	27.7	26.2	104.8	100.8
30	50	32.7	31.2	104	100
40	50	43.15	41.65	104.1	100.1
50	50	52.9	51.4	102.8	98.8
50	—	53.75	52.25	104.5	100.5

The results obtained by this method thus appear to vary within ± 1.5 per cent of the theoretical value.

Method No. 2.

Inverse Titration with Permanganate.

Direct titration with permanganate as originally described by de Haen is, of course, inapplicable in presence of zinc compounds and thiocyanates. The modification described by Bettel involves two separate determinations:

(*i*) The total reducing power obtained by running the solution to be tested into a measured volume of permanganate, to which sulphuric acid has been added, until the color is discharged.

(*ii*) The reducing power, exclusive of ferrocyanide, which is

obtained by precipitating with an acid ferric salt, filtering, and titrating the filtrate.

The difference of these two determinations is supposed to give the reducing power of the ferrocyanide.

The results obtained when the test was made as directed by Bettel were not at all satisfactory, the end-point in determination (*i*) was by no means sharp, and the complete washing of the precipitate in (*ii*) was a lengthy and troublesome operation. Owing to the high reducing power of thiocyanates as compared with ferrocyanides, the thorough washing of the precipitate in this test is most essential. As, however, the estimation of total reducing power may in some cases be a matter of importance, some tests were made on the first of Bettel's determinations (*Proceedings* Chem. and Met. Soc., S. Africa, Vol. I., p. 166).

Method No. 2 (*a*). *Inverse Titration with Acidulated Permanganate.*—A measured quantity of permanganate solution (approximately N/100) was placed in a white porcelain basin with addition of from 10 to 30 c.c. of 25 per cent sulphuric acid (prepared as in the previous tests, by addition of permanganate until a faint pink tint remained permanent). The solution to be tested, containing known amounts of ferrocyanide, together with the usual impurities, was then run from a burette into the acidulated permanganate until the pink color changed to a faint yellow. When much permanganate was used, the addition of the solution caused the formation of a brown precipitate, in which case no definite finishing point could be observed. This was remedied to some extent by increasing the amount of acid.

Table No. 3. *Results of Method No.* 2 (*a*).

Model Solution B	KCy	0.15%,
	K_2ZnCy_4	0.1%,
	KCyS	0.075%,
	$K_4FeCy_6 \cdot 3H_2O$	0.053%.
Standard Permanganate	Approximately N/100 = 0.316 gram per liter.	

N/100 Permanganate taken. c.c.	Special sulphuric acid 25% by vol. c.c.	Model Solution B required. c.c.	N /100 $KMnO_4$ consumed per 100 c.c. B. c.c.	Reducing power % 554=100
30	10	5.5	545	98.4
40	10	7.1	563	101.6
50	10	9.2	543	98
100	20	17.9	559	100.9
100	30	17.8	562	101.4

Similar sets of tests were made with various different mixtures, giving in most cases results varying within ± 2 per cent of the theoretical values.

The N/100 permanganate solution does not retain its strength for any length of time, and requires to be standardized at frequent intervals (on iron or pure ferrocyanide).

Method No. 2 (b). Determining Excess of Permanganate with Potassium Iodide and N/100 Thiosulphate.—As before, the solution to be tested was run into a measured volume of approximately N/100 permanganate, acidulated with from 10 to 30 c.c. of "special" sulphuric acid, but the permanganate was allowed to remain in excess. About 2 c.c. of 1 per cent potassium iodide solution were then added, and the liberated iodine titrated by means of N/100 sodium thiosulphate (2.48 grams $Na_2S_2O_3 \cdot 5H_2O$ per liter). The amount of thiosulphate required is then deducted from the equivalent amount of permanganate originally taken, the difference giving the amount of permanganate reduced by the solution tested.

Table No. 4. Results of Method No. 2 (b).

Model Solution C

KCy	0.15%,
K_2ZnCy_4	0.1%,
KCyS	0.075%,
$K_4FeCy_6 \cdot 3H_2O$	0.152%.

Permanganate taken. c.c.	Equivalent to N/100 permang. c.c.	Model solution C taken. c.c.	N/100 thiosulphate required. c.c.	N/100 $KMnO_4$ consumed. c.c.	N/100 $KMnO_4$ consumed per 100 c.c. of C. c.c.	Reducing power per cent. 434=100
50	45.1	4	27.45	17.65	441	101.6
50	45.1	5	23.4	21.70	434	100
50	45.1	6	19.35	25.75	429	98.9
50	45.1	7	14.7	30.40	434	100
50	45.1	8	10.4	34.70	434	100
50	45.1	9	6.2	38.90	432	99.5

The results obtained by this method generally agreed with about 3 per cent of the theoretical numbers, in some cases the agreement was much closer; in one set the divergence amounted only to 0.5 per cent. It is essential that the permanganate solution should be standardized on the N/100 thiosulphate immediately before or after making the required determinations. The finishing point is ascertained by adding a few drops of starch solution, either freshly prepared or preserved by the addition of a little caustic soda. The blue color generally shows some tendency to return on standing, but the reaction may be considered complete when the solution remains quite colorless for a minute.

The amount of permanganate apparently consumed in oxidizing the various oxidizable ingredients in the solution was considerably less in this method than in Method No. 2 (*a*) (Bettel's form), as shown in the following comparative results:

Table No. 5.

Model Solution D

KCy	0.15%,
K_2ZnCy_4	0.1%,
KCyS	0.075%,
$K_4FeCy_6 \cdot 3H_2O$	0.158%.

Volume of permanganate taken. c.c.	Method No. 2 (*a*).		Method No. 2 (b)	
	Model solution D. required. c.c.	$KMnO_4$ per 100 c.c. of D	Model solution D. required. c.c.	$KMnO_4$ per 100 c.c.of D. c.c.
40	7.5	533	8.6	464
50	9.2	543	10.5	478
60	11.7	513	13.2	455

Method No. 3.

Precipitation as Prussian Blue.

This operation is involved as a necessary step in Bettel's method (described above) and in Erlenmeyer's and Knublauch's methods. In Bettel's method the precipitate of Prussian blue is not dissolved again, but it must be washed and the filtrate titrated with permanganate. In the other methods the precipitate is treated with alkali, and the resulting ferrocyanide titrated, after acidulating, with permanganate or copper sulphate respectively.

Method No. 3 (*a*) (*Erlenmeyer's*). *Precipitation as Prussian Blue, Conversion into a Soluble Ferrocyanide and Titration of the Latter with Permanganate.*—The mixture containing known quantities of KCy, KCyS, K_2ZnCy_4 and K_4FeCy_6 was heated to boiling and poured into 10 c.c. of special ferric chloride solution, also boiling. This special solution contained about 6 per cent of ferric chloride and 20 per cent hydrochloric acid.

The mixture was stirred and allowed to settle, then washed by decantation, and finally collected on a filter and washed thoroughly with boiling water till the washings were free from chlorine and thiocyanates. The precipitate was then washed off the filter paper as far as possible into a clean flask, and 10 c.c. of 5 per cent caustic soda passed through the funnel into the same flask. This was then boiled for some time until the Prussian blue appeared to be completely decomposed, and filtered through the same filters. The ferric hydrate precipitate was then washed until free from ferrocyanide, and the filtrate acidulated by the addition of 10 c.c. 25 per cent sulphuric acid. The resulting liquid was titrated with N/100 permanganate.

The method is long and tedious, as great care must be taken in the washing of both precipitates, which must be done with very hot water.

Attempts made to determine the ferrocyanide by redissolving the ferric hydrate precipitate and treating as in Method No. 1 (*b*) did not give satisfactory results.

Table No. 6. *Results of Method No.* 3 (*a*).

Model Solution E { KCy 0.15%, K_2ZnCy_4 0.2%, KCyS 0.05%,

Ferrocyanide solution N/100 = 0.422%.

N/100 ferrocyanide taken. c.c.	Model solution E added. c.c.	Permanganate required c.c.	Permanganate per 100 c.c. of c.c. N/100 ferrocyanide.	Percentage results 102.8 = 100.
10	50	10.1	101	98.2
20	50	20.95	104.7	101.9
25	50	25.3	101.2	98.4
30	50	31.1	103.6	100.9
40	50	39.9	99.7	97.0
50	50	53.2	106.4	103.5

These results show a variation from the mean value of ± 3.5 per cent.

As the method is scarcely, if at all, more rapid than Method No. 1, it does not appear to present any special advantages.

Method No. 3 (*b*) (*Knublauch's*). *Precipitation as Prussian Blue, Conversion into a Soluble Ferrocyanide, and Titration of the Latter with Copper Sulphate and Ferric Indicator.*—The operations are practically the same as in Erlenmeyer's method, but after acidulating the final filtrate with sulphuric acid, the liquid is titrated by running in copper sulphate (about 1 per cent $CuSO_4 \cdot 5H_2O$) until a drop of the liquid no longer gives a blue color with a drop of dilute ferric chloride, when the two drops are allowed to run into one another on white filter paper. Only a few tests were made by this method, which presents all the drawbacks of Erlenmeyer's method, with the additional disadvantage that the final titration requires an external indicator.

Table No. 7. Results of Method No. 3 (*b*).

Solutions Tested.*				Special 6% ferric chloride taken c.c.	$CuSO_4$ (about 1%) required. c.c.	$CuSO_4$ per gram. ferrocyanide. c.c.	Percent. results 74.1 = 100
Ferrocyanide. gram.	KCy gram.	KCyS gram.	K_2ZnCy_4 gram.				
0.105	0.093	0.03	0.02	10	7.6	72.4	97.7
0.211	0.037	0.03	0.01	10	16.0	75.8	102.3

* 80 c.c. of liquid in each case.

Method No. 4.

Direct Titration with Copper Sulphate.

This method, due to E. Bohlig, is described by Fresenius (*Quant. Anal.*, 7th ed., Vol. I., p. 380). It was found to give moderately good results in absence of zinc, but the presence of this element entirely vitiates the test.

Some of the results obtained in absence of zinc are given below. A modification of the method was also tried in which the zinc was removed by preliminary treatment with sodium sulphide.

Method No. 4 (*a*). *Direct Titration with Copper Sulphate in*

Absence of Zinc.—A measured volume of the solution was acidulated with sulphuric acid, and titrated with 1 per cent solution of copper sulphate, until a drop of the liquid taken out on a glass rod and placed on filter paper beside a spot of very dilute ferric chloride no longer showed any blue coloration. The ordinary white filter paper was found to contain sufficient iron to give a distinct blue color as long as a considerable excess of ferrocyanide was present, but the exact finishing point was determined by means of the ferric chloride solution.

Table No. 8. *Results of Method No.* 4. (*a*).

Contents of Solution Tested.			Volume of 25% H_2SO_4 added.	$CuSO_4$ required.	$CuSO_4$ per gram of ferrocy.	Percentage results. 81.1 = 100
Ferrocyanide. gram.	Cyanide KCy gram.	KCyS gram.	c.c.	c.c.	c.c.	
0.211	0.087	—	4	16.4	77.7	95.2
0.211	0.087	—	4	17.5	82.9	102.2
0.211	0.175	—	4	17.0	80.6	99.4
0.211	—	.06	4	17.5	82.9	102.2
0.211	—	.06	4	17.0	80.6	99.4
0.211	—	.03	4	17.0	80.6	99.4
0.042	0.069	.03	4	3.5	83.3	102.7
0.105	0.027	.03	4	8.5	81.0	99.9
0.211	0.069	.03	4	17.0	80.6	99.4

These results, excluding the first, show values varying within ± 3 per cent of the theoretical amount. The result does not appear to be affected by variation within moderate limits in the amount of cyanide and thiocyanate present.

In presence of zinc the results were always too low, probably owing to the conversion of a part of the ferrocyanide in the acidulated liquid into ferrocyanide of zinc. The following modification was therefore tried:

Method No. 4 (*b*). *Treatment with Sodium Sulphide to Remove Zinc, and Titration of the Filtrate with Copper Sulphate.*—A measured volume of the solution to be tested was mixed with strong alkali and an excess of sodium sulphide solution, well agitated, filtered, and the precipitate of zinc sulphide washed until apparently free from ferrocyanide. The filtrate was then agitated with lead carbonate to remove excess of sulphide, filtered again, washed, and the filtrate acidulated with sulphuric acid, and titrated as above with 1 per cent copper sulphate, and dilute ferric chloride as external indicator.

The precipitate of lead sulphide appeared to carry down a little

ferrocyanide which was not easily washed out; also some lead dissolved in the strongly alkaline liquid, and was precipitated as sulphate on acidulating. The addition of strong alkali was found to be necessary to ensure the complete precipitation of the zinc. The results were not very satisfactory, the following figures showing a variation of ± 6 per cent or more.

Table No. 9. Results of Method No. 4 (b).

Contents of Solution Tested.				H_2SO_4 25% by vol. added.	$CuSO_4$ 1% required.	$CuSO_4$ per 100 c.c. of ferrocy.	Percentage results. 32.7 = 100
$K_4FeCy_6.3H_2O$ 0.422	KCy 0.373%	KCyS 0.3%	K_2ZnCy_4 0.38%				
c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	
25	20	25	20	10	8.7	34.8	106.4
30	25	20	30	10	9.4	31.3	95.7
50	10	10	25	10	15.7	31.4	96.0
50	10	10	10	10	16.5	33.0	100.9
50	15	5	20	10	16.6	33.2	101.5

Method No. 5.

Conversion into Ferricyanide and Titration with Copper Sulphate.

In the method described by F. Hurter, the solution is oxidized by bleaching powder, warmed to drive off excess of chlorine, and the resulting liquid titrated with copper nitrate using ferrous sulphate as external indicator.

This process was slightly modified in both the methods given below.

It was not found advisable to heat the solution, as a blue precipitate formed when the liquid was heated slightly above 140° F., and in this case the results were too low. As heating at this temperature did not readily remove the excess of chlorine, a brisk current of air was aspirated through the liquid for about ten minutes.

In the second modification, permanganate was used instead of bleaching powder as the oxidizing agent.

Method No. 5 (a). Treatment of the Acidulated Solution with Bleaching Powder, and Titration with Copper Sulphate and Ferrous Indicator.—The solution to be tested (containing ferrocyanide, cyanide, thiocyanate and zinc double cyanide) was acidulated by the addition of 10 c.c. 25 per cent sulphuric acid, and a strong solution of bleaching powder (containing from 1 to 2.5 per cent of available chlorine) was added in the cold until a drop of the mixture no longer

showed any blue color with dilute ferric chloride in spots on a porcelain plate. In presence of much zinc a precipitate formed, which, however, redissolved in excess of bleaching powder. Air was then aspirated through the solution by placing it in a flask, with a tube connected with a large jar filled with water, so arranged that by siphoning the water from the jar a brisk current of air was drawn through the liquid in the flask for about 10 minutes. By this means the excess of chlorine was practically removed. The presence of a moderate excess of chlorine did not appear to affect the result materially, but the cyanogen chloride attacks the eyes and renders the manipulation very unpleasant, so that it is advisable to remove it.

The liquid was then titrated with copper sulphate (1 per cent $CuSO_4 \cdot 5H_2O$) using ferrous-ammonium sulphate in spots on a porcelain plate as external indicator, until a drop of the liquid taken out on a glass rod no longer gave a blue color but produced a slight brownish or purplish tinge. The reaction was considered to be complete when the spots became momentarily blue on mixing, but showed no trace of blue after standing for a few seconds. With practice this point could be determined within about 0.2 c.c. of the copper solution.

Experiments in which the liquid was warmed to 140° F. before aspirating gave less satisfactory results.

Table No. 10. *Results of Method No.* 5 (*a*).

			F.	*G.*
Model Solutions	Cyanide	KCy	0.192%	0.105%
	Zinc double Cy	K_2ZnCy_4	0.076%	0.057%
	Thiocyanate	KCyS	0.03 %	0.06 %

Ten c.c. of sulphuric acid (25% by volume) added in each test.

(*i*) *Results with Aspiration.*

Ferrocyanide 0.422% c.c.	Model Solution F taken. c.c.	Bleaching powder solution (about 1%) chlorine. c.c.	$CuSO_4$ required. c.c.	$CuSO_4$ per 100 c.c. of ferrocy. c.c.	Percentage results. 29.6 = 100
15	50	30	4.25	28.3	95.6
20	50	30	5.6	28.	94.6
25	50	30	7.6	30.4	102.7
30	50	50	9.3	31.	104.7
40	50	50	11.85	29.6	100.
50	50	40	15	30.	101.4

(*ii*) *Results without Aspiration.*

Ferrocyanide .422 % c.c.	Model Solution G. taken. c.c.	Bleaching Powder 2.55% Cl. c.c.	$CuSO_4$ required. c.c.	$CuSO_4$ per 100 c.c. c.c.	Percentage results. 31.2 = 100
20	50	10	6.2	31.	99.4
25	25	10	7.8	31.2	100.
25	50	20	7.7	30.8	98.7
40	50	15	12.75	31.8	101.9
50	25	10	15.6	31.2	100.

The first set of tests give results within about ± 5 per cent of the theoretical number, while the second agree within less than ± 2 per cent. It must be remarked, however, that the standard of the copper solution was different in the two series.

Experiments made with widely varying amounts of KCy, K_2ZnCy_4 and KCyS gave very divergent results; nevertheless, the method is so rapid, as compared with any process depending on the complete decomposition of the cyanogen compounds, that it may very possibly be found of use in practice, and if the copper solution be standardized on a liquid of somewhat similar composition to that which is to be examined, the results are sufficiently accurate. If standardized on pure ferrocyanide, the amount of copper required is considerably higher than that necessary with an impure solution containing the same amount of ferrocyanide. Thus in the last series, 50 c.c. of N/100 ferrocyanide with 10 c.c. of the bleaching powder, required 32.5 c.c. instead of 31.2, corresponding to a difference of over 4 per cent.

Method No. 5 (*b*). *Treatment of the Acidulated Solution with Permanganate, and Titration of Liquid with Copper Sulphate and Ferrous Indicator.*—After acidulating with, say 10 c.c. of 25 per cent sulphuric acid, permanganate solution, generally about decinormal, was run in until a slight coloration remained permanent, indicating that all reducing agents were oxidized and the whole of the ferrocyanide converted into ferricyanide. The liquid was then titrated with copper sulphate and ferrous ammonium indicator as in method 5 (*a*).

When very large quantities of reducing agents were present, so that much permanganate was required, a dark brown precipitate occurred which interfered somewhat with the test; in such cases less than the theoretical amount of copper sulphate was required.

Zinc appeared to interfere considerably, rendering the results much too low. Some results are given below in which the zinc was

removed by precipitation as sulphide after making strongly alkaline and heating. The filtrate was then acidulated; oxidized by permanganate and titrated with copper sulphate, as above.

Table No. 11. *Results of Method No.* 5 (*b*) *in Solutions Free from Zinc.*

Model Solution H	$K_4FeCy_6 \cdot 3H_2O$	0.253%
	KCyS	0.030%
	Na_2S	0.013%

Varying amounts of cyanide were added as shown below:

Ten c.c. of 25 per cent sulphuric acid were added in each test, and the permanganate solution (about N/10) was run slightly in excess of the amount required to give a distinct red color.

100 c.c. of mixture H = 60 c.c. N/100 ferrocyanide.

The results appear to be unaffected by variation in the amount of cyanide, but the copper solution should be standardized on a mixture of similar composition to the liquid to be tested.

Table No. 11.

Volume of model solution H taken. c.c.	Cyanide 0.672% KCy added. c.c.	$KMnO_4$ (approx. N/10) c.c.	$CuSO_4$ required. c.c.	$CuSO_4$ per 100 c.c. N/100 ferro. c.c.	Percentage results. 31.4=100
50	—	23	9.4	31.3	99.7
60	10	30	11.3	31.4	100
50	15	23	9.4	31.3	99.7
50	15	30	9.6	32	101.9
50	20	25	9.2	30.7	97.8
50	30	25	9.3	31	98.7
50	30	22	9.4	31.3	99.7
50	35	25	9.7	32.3	102.9
50	40	21	9.5	31.7	101

These results show a variation of ± 3 per cent from the theoretical value. Similar tests with varying amounts of ferrocyanide gave a variation not exceeding 9 per cent.

Table No. 12. *Tests by Method No.* 5 (*b*), *in which zinc was originally present, but was removed by preliminary treatment with sodium sulphide.*

The following test-solutions were prepared:

No. of Test Solution.	Ferrocyanide $K_4FeCy_6.3H_2O$ %	K_2ZnCy_4 %	KCyS %	KCy %
1	0.0422	0.057	0.015	0.10
2	0.0633	0.038	0.06	0.05
3	0.0844	0.095	0.045	0.05
4	0.1055	0.057	0.03	0.125
5	0.1688	0.038	0.045	0.10
6	0.2110	0.076	0.03	0.075

The results of tests with these solutions are shown below:

Table No. 12.

No. of test solution.	Na_2S 0.185% added. c.c.	NaOH 10% added. c.c.	Added to Filtrate.			$CuSO_4$ per 100 c.c. N/100 ferrocy. c.c.	Percentage results. 30 = 100
			$KMnO_4$ 3% c.c.	H_2SO_4 25% c.c.	$CuSO_4$ required. c.c.		
1	20	10	10	20	3	30	100
2	10	10	3.7	20	4.5	30	100
3	25	10	4.5	20	6.2	31	103.3
4	15	10	3	20	7.2	28.8	96
5	15	10	4	20	11.95	29.9	99.7
6	25	10	5.8	20	15.05	30.1	100.3

These numbers show a variation of about ± 4 per cent.

Method No. 6. (Müller's Method.)

Titration with Zinc Sulphate.

A measured quantity of the solution to be tested was acidulated with sulphuric acid, and titrated with zinc sulphate (0.25 per cent Zn); the end-point was determined as in Bohlig's method (No. 4), by placing a drop of the liquid on white filter paper, the exact finishing point being found by means of a dilute solution of ferric chloride. When this ceased to show the slightest blue tint, the reaction was considered complete.

The method was found to be useless in presence of zinc double cyanide, and in absence of zinc did not give results even approximately proportional to the amount of ferrocyanide present, although duplicate tests on solutions containing the same amount of ferrocyanide generally agreed very fairly. This variation in the results is possibly due to the existence of several ferrocyanides of zinc, formed under different conditions. The results were not appreciably affected by variation in the amounts of cyanide or thiocyanate.

Table No. 13. *Results of Method No.* 6, *in Absence of Zinc Double Cyanide.*

Mixture Tested.			H_2SO_4 25% by volume added.	$ZnSO_4$ (.25% Zn) required.	$ZnSO_4$ ferrocyanide per 100 c.c. of N/100 ferro.	Percentage results. 39 = 100
N/100 ferrocyanide. c.c.	KCy 0.373% c.c.	KCyS 0.3% c.c.	c.c.	c.c.	c.c.	
25	—	—	4	10.7	42.8	109.8
50	—	—	4	19.4	38.8	99.5
50	—	—	4	19.95	39.9	102.3
50	10	—	4	19.3	38.6	99
50	20	—	4	19.2	38.4	98.5
50	50	—	4	19.6	39.2	100.5
50	—	10	4	19.2	38.4	98.5
50	—	20	4	19.2	38.4	98.5
50	—	25	4	19.05	38.1	97.7
50	—	50	4	19.8	39.6	101.5
50	25	25	4	19.75	39.5	101.3

These results (excluding the first, in which a different amount of ferrocyanide was used) show a divergence of not more than ± 2.5 per cent. The method, however, cannot be recommended, owing to the irregularities occurring with varying amounts of ferrocyanides.

When zinc double cyanide is present, a partial precipitation of the ferrocyanide as Zn_2FeCy_6 occurs on acidulating with sulphuric acid, hence only the portion still remaining in solution is indicated on titrating with zinc sulphate.

Method No. 7.

Green's Method.

This method is described incidentally in a system of tests designed principally for the estimation of cyanide, alkali and zinc, and published by Leonard M. Green (*Proceedings* Inst. Min. and Met., Oct., 1901). It involves the execution of the other tests. Some of these latter are useful and give results agreeing satisfactorily with theory, but the method of determining ferrocyanide is too involved and indirect to be of much practical value. The results showed only a very rough approximation.

There are four operations, as follows:

(1) Total cyanide is determined by taking *n* c.c. of the solution to be tested, adding 5 c.c. of strongly alkaline potassium iodide solution (say, 4 per cent NaOH and 1 per cent KI), titrating with

silver nitrate until a distinct yellow turbidity remains permanent on shaking. Result = T.

(2) Take again *n* c.c. of the solution to be tested, add one or two c.c. of neutral potassium chromate, and titrate till the liquid remains permanently red on shaking. (Where much free alkali is present this must be carefully neutralized before making this test.) Result = N.

(3) Take *n* c.c. of the solution to be tested. Add 2T c.c. of silver nitrate, then phenol phthaleïn and sodium carbonate till distinctly red. Then exactly neutralize by adding nitric acid drop by drop, shaking and allowing to settle, until the liquid becomes quite colorless. Then add ferrocyanide in excess (say, about 25 c.c. of N/10 solution), which causes the solution to become alkaline again. Titrate with N/10 nitric acid until the color is discharged, leaving a slightly yellowish liquid. The nitric acid must be run in slowly, with constant agitation toward the end. Result of last titration = A.

(4) Take *n* c.c. of the solution to be tested, add N c.c. of silver nitrate, and proceed exactly as in (3). Result = B (proportioned to zinc present).

The quantity B — A should be proportional to the ferrocyanide in the original solution.

Table No. 14. *Results of Method No.* 7.

25 c.c. N/10 ferrocyanide added during each test.

Model Solution J

$K_4FeCy_6 \cdot 3H_2O$	0.1%
KCy	0.2%
KCyS	0.1%
K_2ZnCy_4	0.4%

Vol. of model solution J taken.	Results of Tests.				B — A	B — A per 100 c.c. of J	B — A Percentage results. 5.93 = 100
	(1) T $AgNO_3$	(2) N $AgNO_3$	(3) A HNO_3	(4) B HNO_3			
c.c.	c.c.	c.c.	c.c.	c.c.	c.c.		
15	18.5	33.75	3.05	3.75	0.7	4.7	79.3
20	24.4	57.8	4.1	5.2	1.1	5.5	92.7
25	30.3	73.4	4.6	5.85	1.25	5.0	84.3
30	36.45	86.9	5.65	7.4	1.75	5.9	99.5
40	48.9	116.35	7.15	9.55	2.4	6 0	101.2
50	61	143.4	8.5	11.45	2.95	5.9	99.5

In the first three tests the quantities of nitric acid which have to be determined are probably too small for accurate measurements under the conditions of the test.

CONCLUDING REMARKS.

Of the different methods examined, that described under 1 (*b*) gave the most closely concordant results, and with care could no doubt be applied with great accuracy for the determination of ferrocyanides under ordinary conditions. It is, however, decidedly too long for general use in cases where determinations have to be made at frequent intervals.

For rapid approximate results, Hurter's method (No. 5 (*a*)) with the modifications herein described, appears to be the most serviceable. It is, however, absolutely essential that the standard copper solution should be standardized on a liquid (containing an exactly known quantity of ferrocyanide), and having other ingredients approximately in the proportions which may be expected to occur in the liquid to be examined.

The investigation is far from complete, and many tests were made on various minor points to which no reference has been possible in this paper. In the results which are here presented, however, every effort has been made to eliminate the personal element; whenever possible, the solutions were prepared by one operator, and tested by another who was not previously informed of their composition. It is hoped, therefore, that the data which have been obtained may serve as a useful basis for further researches.

APPENDIX. CLASS I.

Estimation of Free Cyanide.

Method No. 6.

Estimation of Free Cyanide by Distillation with Magnesium Chloride.

W. Feld (*Journ. f. Gasbeleucht.*, XLVI. [29] 561; see also J. S. C. I., September 30, 1903) has shown that if cyanides of the alkalis, of ammonium or of the alkaline earths are distilled with solutions of certain neutral salts, preferably magnesium chloride or lead nitrate, the cyanogen is expelled quantitatively as HCy:

(*a*) $MgCl_2 + 2KCy + 2H_2O = Mg(OH)_2 + 2KCl + 2HCy$,

(*b*) $Pb(NO_3)_2 + 2KCy + 2H_2O = Pb(OH)_2 + 2KNO_3 + 2HCy$,

and has applied these reactions in the estimation of free cyanide in commercial cyanides.

If sulphides be present in the solution to be distilled, lead nitrate should be used, to avoid the evolution of H_2S which occurs when magnesium chloride is employed.

In analyzing a pure alkali cyanide, 0.25 to 0.5 grams of the substance, dissolved in 80 to 100 c.c. of water, is distilled with 5 to 30 c.c. of 3N magnesium chloride solution for about 15 to 20 minutes, with the exit tube of the condenser dipping into 25 c.c. of normal caustic soda solution. The whole apparatus should be gas-tight and should be placed in a good draught chamber. To the liquid containing the distillate there is added about 5 c.c. of a 4% solution of KI and the cyanide is then titrated in the ordinary way with $AgNO_3$. The results are said to be accurate, and not influenced by the presence of ferrocyanides, of thiocyanates or (if lead nitrate be used) of sulphides.

Estimation of Total Cyanide.

Method No. 5.

Estimation of Total Cyanide by Titration with Mercuric Chloride and Potassium-mercuric Iodide Indicator.

L. M. Green (*M. Sci. Press*, January 28, 1905) describes the following modification of Hannay's method, which makes it

applicable for the determination of cyanide in presence of impurities such as zinc, ferrocyanides, etc., which ordinarily interfere. In place of ammonia, a solution of potassic mercuric iodide is used, which gives exceedingly good results and a sharp end-point when a cyanide solution is titrated with mercuric chloride. The end-point is shown by the appearance of a scarlet precipitate of mercuric iodide. This precipitate is somewhat soluble in, and its color is affected by, caustic alkalis, but is not affected by carbonates or bicarbonates. Hence it is necessary where hydrates are present to add excess of bicarbonate before testing. In the presence of zinc double cyanide the whole of the cyanogen in combination with the zinc is estimated, but when double cyanides of copper are present, the whole of the cyanogen is not determined unless an excess of ferrocyanide be also added.

The *standard solution* recommended contains 10.422 grams $HgCl_2$ per liter.

The *indicator* is prepared by dissolving 1 gram KI in water, adding $HgCl_2$ solution till a permanent pink tinge is produced, then 2 grams each of potassium ferrocyanide and sodium bicarbonate, making up to 200 c.c. with water. 10 c.c of the indicator are used for each test.

By combining this method of titration with the ordinary silver nitrate method it is possible to determine the amount of cyanide combined with copper, and a further modification gives a means of estimating zinc. [See Class VII. Base metals.]

Estimation of Total Cyanogen.

Method No. 5.

Determination of Total Cyanogen by Boiling with Magnesium Chloride and Mercuric Chloride.

W. Feld (*Journ. f. Gasbeleucht.*, XLVI [29] 561; J. S. C. I, September 30, 1903) has shown that mixtures containing cyanides, ferrocyanides and ferricyanides may be analyzed by boiling with a mixture of magnesium and mercuric chlorides and subsequently distilling with hydrochloric or sulphuric acid. An excess of alkali is mixed with the solution to be analyzed before adding the reagents. The reactions are:

(*a*) $MgCl_2 + 2NaOH = Mg(OH)_2 + 2NaCl$

(*b*) $2K_4FeCy_6 + 8HgCl_2 + 3Mg(OH)_2 = 6HgCy_2 + Hg_2Cl_2 + Fe_2(OH)_6 + 3MgCl_2 + 8KCl$

or analagous reaction in the case of other cyanogen compounds.

In analyzing *pure soluble salts* containing no free cyanide 0.3 to 0.5 gram of the substance is dissolved in 100 to 150 c.c. of water. 10 c.c. of normal caustic soda are added, and to the boiling solution, 15 c.c. of 3N magnesium chloride are added very slowly to avoid formation of clots of $Mg(OH)_2$. To the boiling mixture about 100 c.c. of boiling N/10 mercuric chloride solution are added and the whole is boiled for 5 to 15 minutes. The liquid is then distilled with the addition of 30 c.c. of 4N hydrochloric or sulphuric acid, the HCy being collected in NaOH solution and titrated with $AgNO_3$ in the ordinary way, using KI indicator.

In analyzing *mixtures containing free cyanide* a portion containing 0.5 to 2 grams of the cyanogen compounds is mixed intimately with 1 c.c. of normal ferrous sulphate, and 5 c.c. of 8N caustic soda, and analyzed exactly as above.

When *sulphides* and *thiocyanates* are present, the distillate becomes slightly turbid on account of the presence of free sulphur, and can with difficulty be titrated with $AgNO_3$. This trouble is overcome by agitating the distillate with lead carbonate, filtering and titrating an aliquot part of the filtrate. In presence of thiocyanates H_2SO_4 should be used for the distillation in preference to HCl, as with the latter the results are much too low.

Method No. 6.

Determination of Total Cyanogen by Boiling with Oxide of Mercury and Reducing with Aluminium.

V. Borelli (*Gaz. chim. ital.*, 1907, XXXVII. [1] 429; see also J. S. C. I., September 30, 1907, p. 1030) gives the following, for determining cyanogen in complex iron-cyanogen compounds. The substance or solution is heated with excess of yellow mercuric oxide, filtered, and the filtrate made strongly alkaline with NaOH. Commercial aluminium powder, free from halogens, is then added with vigorous agitation. For each gram-molecule of mercury, 12 to 15 gram-molecules of NaOH and 4 to 5 gram-molecules of Al are used, the latter being added at intervals of 10 to 15 minutes during the course of 2 or 3 hours. When reduction is complete, the solution is filtered, and the cyanogen which is now present as sodium cyanide, determined by the ordinary methods. Chlorides, bromides, iodides, and thiocyanates do not interfere.

Qualitative Tests for Cyanide.

Detection of Traces of Cyanide.

Method No. 1.

The following method is given by G. W. Williams (*Journal* Chem. Met., and Min. Soc. of S. Africa, IV., 412):

"Evaporate 500 c.c. of the suspected solution with 3 or 4 drops ammonium sulphide. Bring to dryness on a water-bath and take up with a small quantity of water, or water and alcohol. Filter and add a drop of ferric chloride solution. If cyanide was present in the original liquid a red color is formed (ferric thiocyanate). It is possible to use this for a rough colorimetric estimation of the amount of cyanide. 1 part in 100,000 can be detected, so that the method is serviceable for detecting traces of cyanide in mill water."

Method No. 1a.

A. Whitby (*Journal* Chem., Met and Min. Soc. of S. Africa, August, 1904, p. 54) modifies the process of G. W. Williams as follows:

Add a small crystal of tartaric acid to 500 c.c. of the water in a capacious flask; connect the flask with a bulbed U-tube containing sufficient ammonium sulphide to form a trap. Keep the U-tube cool by immersion in water. Boil the water in the flask for 5 to 10 minutes. All the HCy passes over into the U-tube. Wash out the contents of the latter into a small porcelain dish and evaporate to dryness on a water-bath. Take up with water and add one drop of dilute HCl. Filter into a Nessler glass. Add Fe_2Cl_6 and compare the color with that produced by a standard solution of K CyS.

This test is more rapid than that given by G. W. Williams (No. 1) and has the further advantage that it is applicable when thiocyanates are present in the original liquid; in such a case method No. 1 would of course be inadmissible. According to Williams (*loc. cit.*, p. 56) it is less accurate when very minute traces have to be looked for.

Method No. 2.

Stanley R. Benedict (*Amer. Chem. Journ.*, XXXII., No. 5) describes the following test, which depends on the fact that the

precipitate formed by mercurous salts with excess of sodium hydroxide is affected by cyanides, one portion dissolving, while the color of the remainder changes from black to light gray, owing to reduction to metallic mercury. No such effect is produced by ferrocyanides or thiocyanates. Ferricyanides interfere with the test, but according to the writer, cannot coexist with cyanides.

Mercuric salts give a yellow precipitate with caustic soda, soluble in cyanides but not in ferrocyanides or thiocyanates.

The method of testing recommended is as follows: The solution is made alkaline with NaOH, then about 0.5 to 1 c.c. of N/25 mercurous nitrate is allowed to flow slowly down the side of the tube, so that it will remain at the top. A ring of black mercurous oxide is thus formed. The test tube is now gently agitated so that a mixture of precipitate and solution slowly takes place. If KCN be present a portion of the precipitate will dissolve while the rest will become light gray. The test is said to be very much more delicate than the Prussian blue test. For very delicate work, a blank test is made for comparison, using the same proportions of mercurous nitrate and NaOH as in the actual test.

Method No. 3.

The following, by Thiery, is described in *Journal* Soc. Chem. Ind., February 28, 1907, p. 168.

Absorbent paper, moistened with a 1 : 2000 solution of cupric sulphate is dried and cut into suitable strips. The following reagent is prepared: 0.5 gram of phenol phthaleïn is dissolved in 30 c.c. of absolute alcohol; sufficient distilled water is then added to produce a faint turbidity; then 20 grams of sodium hydroxide are added. Aluminium dust is then mixed with the red alkaline solution a little at a time until the color is discharged. The liquid is next diluted to 150 c.c. with distilled water which has been boiled and cooled without contact with the air. The reagent is then filtered. It keeps indefinitely.

To apply the test, the cupric sulphate test paper is moistened immediately before use with a few drops of the reagent. It will detect the presence of 1 part hydrocyanic acid in 2 million. Hydrogen peroxide, ferric chloride, nitric acid and ethyl nitrate do not give a similar reaction, but liquids containing ammonium

persulphate, hypochlorites, sodium peroxide, or perchlorates give a positive reaction, the color, however, entirely disappearing in a few hours, whereas that given by HCy is permanent for 24 hours.

Estimation of Hydrocyanic Acid.

Method No. 3.

Estimation of Hydrocyanic Acid by Standard Alkali after Addition of Silver Nitrate.

If to a solution containing simple cyanides, zinc double cyanide and hydrocyanic acid a sufficient amount of silver nitrate be added to produce a distinct white turbidity and then an excess of ferrocyanide (say 10 c.c. of a 5% solution of $K_4FeCy_6 \cdot 3H_2O$), the amount of hydrocyanic acid may be estimated with sufficient accuracy for practical purposes by titrating with standard alkali and phenol phthaleïn.

1 c.c. N/100 alkali = 0.00027 gram HCy.

APPENDIX. CLASS II.

Estimation of Protective Alkali.

Criticism of Method No. 1.

With regard to this process, Gerard W. Williams (*Proc.* Chem. Met. and Min. Soc. of S. Africa, Vol. IV., p. 412) states "that for solutions carrying no zinc this process is not strictly accurate, but may be made so by adding a slight excess of silver nitrate, filtering off an aliquot portion, and determining the alkali in the filtered solution. This method gives a clearer end-point and the results are slightly higher and more accurate. Silver cyanide appears to have some slight effect on phenol phthaleïn." [The present writer's experience is that this modification gives results identical with those of the original process; in any case, for practical purposes it appears to be an unnecessary complication.]

Criticism of Method No. 2.

Gerard W. Williams (*Proc.* Chem., Met., and Min. Soc. of S. Africa, IV., 412, May, 1904) criticises this method as follows:

"With 'made up' solutions the results are fairly accurate, but with working solutions they vary considerably, and the variation from the true value is not constant. When K_2ZnCy_4 is precipitated by $AgNO_3$ in the presence of varying quantities of ferrocyanide, too low a value is obtained on neutralizing with acid. Moreover the end-point is not sharp, and the color returns slowly on standing."

Williams (*loc. cit.*) states that more accurate results are obtained by adding silver nitrate, then a known excess of N/10 acid, then ferrocyanide free from alkali, and titrating the excess acid with standard alkali, but even thus the results are too high.

With methyl orange as indicator the results were consistently too high, the true value being usually the mean of those found with phenol phthaleïn and methyl orange. If to a normal working

solution containing, say, .07% of zinc and .06% of K_4FeCy_6 acid is slowly added, a gelatinous precipitate slowly settles out. The composition appears to be $ZnK_2Fe(Cy)_6 + xZnO$, where x is extremely variable and may be almost nothing. As the relative percentage of ferrocyanide is increased, the precipitate approximates to the formula $Zn_2Fe(Cy)_6$ and does not carry down so much ZnO. The precipitate is slimy and hard to filter. On adding a large excess of ferrocyanide, the precipitate is very slow in forming.

The gelatinous precipitate formed when zinc is in excess collects the coloring matter of the indicator (methyl orange) and on filtering this is entirely removed. Moreover, by reflected light the methyl orange entangled in the precipitate appears pink, when by transmitted light its color is still yellow. The use of excess of ferrocyanide removes all difficulties, and all titrations should be made under such conditions.

Note on the Behaviour of Zinc Ferrocyanide in Reference to Alkalinity Determinations

Gerard W. Williams (*Proc.* Chem., Met., and Min. Soc. of S. Africa, Vol. IV., p. 412) points out that one of the greatest drawbacks to Green's method is the tendency of zinc ferrocyanide to form precipitates of varying composition. Zinc forms a long series of ferrocyanides some of which are basic, or carry down ZnO mechanically. The nature of the precipitate varies with the quantities of the reagents present and also as to whether the precipitation takes place in neutral, alkaline or acid solution. When acid is slowly added to a cyanide solution containing zinc and ferrocyanide, the following changes occur:

Ferrocyanide present per 1 part of zinc	Nature of Precipitate	Result of Alkali Titration
0 to 3	Flocculent	Too low
3 to 5	Milky, difficult to filter	Color-change difficult to observe in turbid solution
5 and over	No precipitate for 3 or 4 minutes; forms slowly; white and slimy, impossible to filter	Accurate if determined prior to formation of precipitate

The nature of the precipitate varies according to the relative amounts of zinc and ferrocyanide in the solution. As obtained by Green's method it is basic, for which reason the pink color

continues to return slowly after several additions of acid. If the solution be filtered (no easy matter) the clear liquid gives a lower value than the unfiltered solution.

"In made-up solutions, Green's method gives fairly concordant results, if full time be allowed for the end-reaction, but in working solutions it gives indifferent results, perhaps owing to the presence of organic bodies such as amines."

Method No. 2a.

Indirect Titration of Alkali after Addition of Silver Nitrate.

The following modification of Methods 1 and 2 is proposed by Gerard W. Williams (*loc. cit.*):

(*a*) *In absence of zinc.*

(i) Determine total cyanide in the ordinary way.

(ii) To 50 c.c. of the solution add sufficient $AgNO_3$ to precipitate 75 per cent of the total cyanide, then excess of N/10 HNO_3 (say 10 c.c., but when much alkali is present more may be required). Then add sufficient $AgNO_3$ to precipitate the rest of the cyanide. A small excess does not matter. Make up to 100 c.c. and filter off 75 c.c. Determine excess of acid by N/10 alkali and methyl orange. The alkalinity so found is the equivalent of total hydrates and carbonates. (In certain solutions it is possible by adding excess of ferrocyanide to the acid solution, to determine alkalinity to phenol phthaleïn, which gives a sharper end-point. The alkali value is the same whether phenol phthaleïn or methyl orange be used.)

(*b*) *In presence of zinc.*

(i) To 25 c.c. of the working cyanide solution add 5 c.c. N/10 ferrocyanide and 3 drops of the methyl orange indicator. Titrate rapidly in duplicate with standard acid, using one lot as a color-check against the other. Observe color change against a white background, and titrate till a distinct change is observed.

(ii) Titrate the second lot, adding acid rapidly to within 1 c.c. of the amount previously required. Then titrate drop by drop. The result obtained will probably be lower than the first by about 0.2 to 0.4 c.c. The second result should be taken.

(iii) The "total cyanide" is determined in the ordinary way by titrating with $AgNO_3$ in presence of alkali and KI.

If y = no of c.c. N/10 acid required by 25 c.c. of solution taken in test ii. (total alkali)

t = no of c.c. N/10 $AgNO_3$ for 50 c.c. solution in test iii. (total cyanide)

then

4 (y — t) = c.c. of N/10 protective alkali for 100 c.c. of solution tested.

4 (y—t) × 0.004 = percentage of protective alkali calculated as NaOH.

[It should be noted that the "protective alkali" thus obtained includes the total value of carbonates, and thus gives too high a result (see p. 61). Green's method, however, gives the true value as against atmospheric CO_2, and should therefore be used in preference to the above whenever it gives a definite end-point.]

Estimation of Carbonates.

Gerard W. Williams (*Proc.* Chem., Met., and Min. Soc. of S. Africa, Vol. IV., p. 412) applies this method as follows for the accurate determination of carbonates: "Shake up 250 c.c. of solution with 2 or 3 grams barium chloride. Allow to stand, with frequent shakings, for about an hour. Filter; pass the first filtrate through the paper till quite clear. Rinse out flask into filter. Wash well. With a glass rod perforate base of filter and wash precipitate into flask. Place filter paper also in flask and add slight excess of N/10 HCl or H_2SO_4. Warm to about 90° C. and determine residual acid by N/10 alkali."

Calcium chloride cannot be advantageously used instead of barium chloride; it does not precipitate the carbonate in presence of cyanide below 90° C., and the precipitate is fairly soluble in the solution even at that temperature; moreover, on warming a cyanide solution to 90° C. with calcium salts, particularly with excess of lime, a certain amount of carbonate is produced by decomposition of the cyanide, hence the result obtained is too high. Addition of alkalis (KOH or NaOH) retards this decomposition.

A. Whitby, however (*Journal* Chem., Met., and Min. Soc. of S. Africa, August, 1904, p. 54), states that carbonates in solution may be determined by adding a drop or two of dilute ammonia

and then a solution of calcium nitrate, filtering quickly, and washing with hot water. This statement is criticised by Williams (*loc. cit.*) on the ground that $CaCO_3$ is soluble with decomposition in cyanide solutions at normal temperature.

APPENDIX. CLASS III.

Estimation of Ferrocyanides.

Estimation of Ferrocyanide by Determining Cyanogen after Decomposition of Ferrocyanogen by Means of Mercury Compounds.

W. Feld (*Journ. f. Gasbeleucht.* XLVI. [29] 561; see also *Journal* Soc. Chem. Ind., September 30, 1903) uses the following method for determining the *soluble iron-cyanogen compounds* in crude cyanide materials. The latter are first treated in the cold with a solution of magnesium chloride. The material must not be boiled or digested with warm water; even pure cold water must not be used, as otherwise a part of the cyanogen would be converted into thiocyanate by the reaction with the sulphur present. The extract is then boiled with the addition of about 0.5 grams of magnesia, to decompose free cyanides and sulphides, and after the gradual addition of caustic soda solution it is boiled with mercuric chloride and distilled with sulphuric acid. The hydrocyanic acid is collected in caustic soda and titrated with silver nitrate and KI indicator in the usual way.

Insoluble pure salts, such as Prussian blue, are decomposed by rubbing 0.5 grams into a cream with 4 to 5 c.c. of water and boiling; 30 c.c. of 3N magnesium chloride solution are next added and the process follows as described for soluble salts.

Insoluble iron-cyanogen compounds, in presence of simple cyanides, are treated as follows: From 0.5 to 2 grams of the substance are rubbed down finely with 1 c.c. of 3N magnesium chloride solution and 2 c.c. of water, and the mixture is derived on the water-bath to expel HCy. The residue, when perfectly cold, is rubbed into a cream with 5 c.c. of 8N caustic soda solution for a few minutes; about 10 c.c. of the $MgCl_2$ solution are slowly added with continuous stirring, and the liquid is transferred to the distilling flask; 20 c.c. more $MgCl_2$ solution are added, the whole diluted to 150 to 200 c.c. and boiled for 5 minutes. To the

boiling solution 100 c.c. of boiling N/10 mercuric chloride solution are added, and after 5 to 10 minutes' boiling the liquid is distilled with the addition of 30 c.c. of 4N sulphuric acid, the titration being carried out as before.

Estimation of Ferrocyanides after treatment with Brominized Caustic Soda.

E. Donath and B. M. Margoshes (*Journ. für prakt. Chem.*, LV. [1899]) give a method applicable for determining ferrocyanide in cases where part of the iron is present in other forms. The substance or solution is digested with 8 per cent caustic soda with gentle warming. The whole or an aliquot part is then filtered, and the filtrate treated with some of the 8 per cent NaOH to which 20 c.c. of bromine have been added. A precipitate of ferric hydrate is thus obtained, representing only that part of the iron which was originally present as ferrocyanide. This is filtered off, dissolved in HCl and re-precipitated with ammonia. Its iron contents may then be determined by any of the ordinary methods.

Estimation of Thiocyanates.

Estimation of Thiocyanates by Titration with Silver Nitrate.

Thiocyanates may be estimated with considerable accuracy *by a reversal of Volhard's method* for the estimation of silver. Ferrocyanides, if present, must first be precipitated by means of an acid solution of ferric sulphate, the excess of which serves as an indicator. The mixture is filtered, and the filtrate titrated with $AgNO_3$ till the red color of the ferric thiocyanate is discharged. The presence of chlorides would interfere with this method; cyanides would presumably be converted into ferrocyanides and finally into Prussian blue and removed by the filtration.

C. J. Ellis ("Notes on Residual Cyanide Solutions," *Journal* Soc. Chem. Ind., February, 1897) recommends precipitating the ferrocyanide as Prussian blue, filtering, precipitating excess of iron by caustic potash, and again filtering. After neutralizing the filtrate, he then determines the thiocyanate by the method of Barnes and Liddle (Chem. of Cyanide Solutions, p. 89, Group D). As an alternative process he uses the colorimetric method given above (*loc. cit.*, p. 89, Group C).

Estimation of Thiocyanates by Distilling with Hydrochloric Acid and Aluminium.

W. Feld *Journ. für Gasbeleucht.*, XLVI. [29] 561; (see also *Journal* Soc. Chem. Ind., September 30, 1903) uses the following:

"Six small coils of sheet aluminium, made of strips about 20 cm. long and 0.5 cm. broad are placed in the flask along with the substance under examination and about 100–120 c.c. of water. Into the boiling solution 20 c.c. of 4N hydrochloric acid are run, and after the violent evolution of hydrogen has ceased, further quantities of acid are added."

The thiocyanate is decomposed as follows:

$$3KCNS + 4Al + 18HCl = 2KCl + 2Al_2Cl_6 + 3NH_4Cl + 3C + 3H_2S.$$

The distillate is received in a vessel containing a measured quantity of iodine solution of known strength, which reacts with the H_2S as follows:

$$H_2S + I_2 = 2HI + S.$$

The distillation is continued, with fresh additions of acid if necessary until no further decolorization of the iodine solution occurs. A gentle stream of CO_2 is maintained during the distillation. Finally the excess of iodine is titrated with standard thiosulphate.

The presence of thiosulphates interferes with this method. In such cases the solution is first boiled with addition of mercuric chloride and sufficient magnesia to render it alkaline. The thiosulphate is completely decomposed as follows:

$$Na_2S_2O_3 + HgCl_2 + MgO = HgS + 2NaCl + MgSO_4,$$

the thiocyanate being unaffected.

When both salts are present, the method used is to boil with a mixture of mercuric and magnesium chlorides and magnesia. After cooling, the liquid is diluted to a definite volume, filtered through a dry filter, and an aliquot portion of the filtrate, which contains the thiocyanate alone, is distilled with HCl and aluminum as described above.

Modification of Colorimetric Method.

In using the method described in the text (see Chem. of Cyanide

Solutions, p. 89, Group C)., F. Hurter (*Chem. News*, XXXIX., 25) recommends the addition of zinc chloride to precipitate ferrocyanides before applying this test. The standard thiocyanate may be adjusted to the required strength by titrating with permanganate as in Method A (Chem. of Cyanide Solutions, p. 87).

Estimation of Seleno Cyanates.

Selenium, when present in cyanide solutions, occurs as selenocyanates (*e.g.*, NaSeCN) analogous to thiocyanates. It may be estimated rapidly, with sufficient accuracy for ordinary purposes, by the following colorimetric method (*Engineering and Mining Journal*, October 28, 1905, p. 777):

100 c.c. of the cyanide solution are mixed with 10 c.c. concentrated HCl and boiled for about 5 minutes. The selenium is completely precipitated, and remains in suspension for some time, the tint of the emulsion varying, according to the amount and nature of other ingredients present, from light orange to bright scarlet. The tint is compared with that of a similar amount of a standard containing a known quantity of selenium. The standard selenium solution may be prepared by dissolving 10 mgr. of pure selenium in concentrated bromine water, adding $NaHCO_3$ till colorless, and making up to a liter. Check solutions are prepared of approximately the same composition as the cyanide solution to be tested, but free from selenium. Measured quantities of the standard selenium are then added to the checks, together with 10 c.c. HCl, and heated to boiling. This is repeated with different amounts of the selenium solution until a tint is obtained corresponding to that of the solution to be tested. In some cases a little sodium bisulphite is added to assist the precipitation of the selenium. In the case of working cyanide solutions at the Redjang Lebong Mine, Sumatra, a close imitation of the tint was obtained by boiling measured volumes of the selenium solution with 5 to 10 c.c. of a 5 per cent solution of $NaHSO_3$, and adding a mixture of 1 vol. potassium ferrocyanide with 5 vols. of a zinc chloride solution equivalent in strength to the ferrocyanide. The boiling must not be continued too long, or the selenium will be precipitated in a dense black form unsuitable for colorimetric estimation.

Copper interferes with the test, as when ferrocyanides are

present a precipitate is obtained consisting of mixed ferrocyanides of zinc and copper, having a tint somewhat similar to that given by selenium.

Estimation of Sulphides.

Method No. 2a.

Colorimetric Estimation of Sulphides by means of Soluble Lead Salts.

C. J. Ellis (*Journal* Soc. Chem. Ind., February, 1897) has shown that small quantities of sulphides in presence of cyanides can be conveniently estimated by means of alkaline lead solutions, such as sodium plumbate. The present writer has frequently used a solution of lead tartrate in caustic soda for the same purpose.

The method as detailed by Ellis is as follows:

The solution is decolorized if necessary. A rough determination of the sulphide is first made colorimetrically by means of the lead solution to find whether it contains more or less than 1 part of sulphide in 20,000.

(*a*) The solution contains less than 1 part in 20,000. It is still further diluted with recently boiled and cooled distilled water until it contains only 4 to 6 parts K_2S per million, which is about the most convenient strength to test. Two quantities of (say) 300 c.c. of this diluted solution are measured into flasks placed on a white surface and successive quantities of 0.5 to 1 c.c. of the lead solution added to each flask until the last addition to one fails to make its contents darker than those of the other. The amount of sulphide is then calculated from the quantity of lead solution employed, omitting this last addition. At first, each addition of lead solution forms a distinct brown cloud. When this is no longer noticed, the end-point is nearly reached. It is stated that 2 to 3 parts of sulphide in 10 million parts of solution can be determined by this means, even when the liquid is originally slightly colored.

(*b*) The solution contains more than 1 part in 20,000. A suitable quantity, say 5 to 100 c.c. according to the amount of sulphide suspected to be present, is put into a flask and the lead solution run in until the precipitate does not increase perceptibly.

About 1 or 2 c.c. is filtered through several thicknesses of filter-paper, the filtrate generally being brownish. Half of it is placed in each of two small test-tubes; a drop or two of the lead solution is added to one test-tube and, if its contents become darker than those of the other, both are returned to the main solution and further lead solution added. The test is then repeated, and so on until no darkening takes place.

The presence of the other constitutents of the solution appears to have no effect on the accuracy of the determination made in this way.

Modified Colorimetric Method for Sulphides.

Gerard W. Williams (*Journ.* Chem. Met. and Min. Soc. of S. Africa, VI., 170, November, 1905) gives the following modification of the above process:

Two lots of 5 grams each of the sample are dissolved in 100 c.c. of previously boiled distilled water. To one lot about 0.5 gram of lead carbonate is added, the solution well shaken for a few minutes, and filtered. This gives a check solution free from sulphides but otherwise similar to the actual sample to be tested, and the effect of any impurities present is thus equalized. 50 c.c. of the solution of the sample are placed in a Nessler's tube and 1 c.c. of alkaline plumbate, prepared by digesting litharge in 5 per cent caustic soda, are added. An equal volume of the check is placed in another similar tube, lead solution added, and a solution of sodium sulphide containing 1 milligram per c.c. is added from a burette until the color in the two tubes is equal. The volume of standard sulphide solution used thus gives the number of milligrams of sulphide (estimated as Na_2S) in 2.5 grams of the sample.

The results are accurate and agree well with those obtained by the nitroprusside method (Chemistry of Cyanide Solutions, p. 92, Method No. 3). They are higher than those given by Method No. 2 (*Id.*, p. 91).

Williams notes that when lead carbonate is digested in a solution of commercial cyanide, minute quantities of lead are dissolved. It is therefore impossible to employ a check solution, prepared as described, in conjunction with the nitroprusside method, as the brown color produced on adding sulphide solution masks the violet of the nitroprusside coloration.

Estimation of Thiosulphates.

Method No. 1.

In absence of other reducing agents, thiosulphates may be simply and accurately estimated as follows:

A measured volume of the solution is exactly neutralized with dilute standard acid, using methyl orange as indicator. The thiosulphate may then be determined by the ordinary method of titration with iodine solution, using starch as indicator. Thiocyanates do not interfere. The method depends on the fact that free hydrocyanic acid is not rapidly oxidized by iodine.

Method No. 2.

The following method is described by A. Gutmann (*Zeit. Anal. Chem.* [1907], VIII., 485; see also *Journal* Soc. Chem. Ind., September 16, 1907, p. 991).

It depends upon the reaction of thiosulphates with alkaline cyanides whereby they are converted into sulphites and thiocyanates:

$$Na_2S_2O_3 + KCy = Na_2SO_3 + KCyS.$$

To a measured volume of the solution are added 1 gram of potassium cyanide and 2 c.c. of a 15 per cent solution of sodium hydroxide, both free from chlorides, and the mixture is heated for half an hour on the water-bath. It is then cooled and made up to 100 c.c. The excess of cyanide is estimated in 20 c.c. of this solution by the ordinary silver nitrate method. A known excess of silver nitrate is then added, together with dilute nitric acid, for the complete precipitation of the thiocyanate, and the residual silver estimated by back titration with standard thiocyanate (Volhard's process). Any thiocyanate originally present must of course be determined and allowed for.

APPENDIX. CLASS V.

Estimation of Cyanates.

Cyanates are not likely to occur in ordinary working solutions, as they would generally be reduced by the nascent hydrogen of the zinc boxes, but their determination in commercial cyanide may be of importance in some cases.

The methods adopted for determining cyanates may be classified as follows:

(1) Methods depending on the reactions of silver cyanate.

(2) Methods depending on the conversion of cyanate into ammonium compounds, and distillation of the latter.

(3) Alkalimetric methods depending on the behavior of cyanates towards mineral acids.

To the first class belong the methods 1, 2 and 3 described, pp. 104–107 of the text.

Method No. 4 (O. Herting), p. 108, belongs to the second class, and is the method which the present writer has generally found most satisfactory. We here give some additional details:

Estimation of Cyanates by Conversion into Ammonium Salts and Distillation.

Two to 3 grams of the salt are dissolved in water in an evaporating dish. A slight excess of hydrochloric acid is then added and the mixture evaporated to dryness on a water-bath under a hood.

The residue is then dissolved in a little water and transferred to a distilling flask connected with a suitable condenser and 2 bulb U tubes or other receivers containing a measured quantity of N/10 acid. A slow current of air is maintained through the apparatus by means of an aspirator. When all is ready, a little strong caustic soda is introduced into the distilling flask and heat applied, boiling gently for some time but without evaporating to dryness. Certain precautions are necessary to prevent spurting, which might carry some of the alkaline liquor from the distilling flask into the receiver. The writer uses a plug of glass

wool suspended over the opening of the exit tube of the distilling flask. When the operation is complete, the residual acid in the receivers is titrated with N/10 alkali and methyl orange.

1 c.c. N/10 acid consumed = 0.004201 grams CNO.

Estimation of Cyanates by Determining Carbonic Acid Evolved on Distillation with Acids.

A method very similar to the preceding is described by Thos. Ewan (*Journal* Soc. Chem. Ind., March 15, 1904, p. 244). The same reaction is used, viz.,

$$RCNO + 2HCl + H_2O = RCl + NH_4Cl + CO_2,$$

but the carbonic acid is determined instead of the ammonia. This is carried out as follows:

About 1 gram of the sample, dissolved in 50 c.c. of water, is brought into a 100 c.c. distilling flask, the side tube of which is bent upwards and sealed into a rod and disc fractionating column about 4 in. long. The upper end of this column communicates with the condenser. This arrangement serves to prevent splashing. The receivers contain a dilute solution of caustic soda and baryta free from carbonate equivalent to 40 to 50 c.c. normal NaOH; a large excess makes it difficult to wash the barium carbonate completely. The pressure within the apparatus is kept slightly below that of the atmosphere during the distillation. Hydrochloric or sulphuric acid is introduced into the distilling flask by means of a tap funnel until the contents are acid to methyl orange, avoiding a large excess. After distilling off 30 to 40 c.c. of liquid the apparatus is swept out by a slow current of air free from carbonic acid. The barium carbonate formed in the receivers is filtered off, washed and titrated with N/10 HCl.

The amount of carbonate present is determined in another portion of the sample by precipitating with barium chloride in the cold,* or the carbonate may be precipitated and filtered off before introducing the solution into the distilling flask.

The residue in the distilling flask can of course be used for a check determination by Herting's method, by simply adding caustic soda and distilling.

The *cyanide* may also be determined in the filtrate from the barium carbonate precipitate.

* And the necessary correction applied in calculating the cyanate.

The author states that "The accuracy is not very great, but is sufficient for most purposes."

The method has the advantage that the preliminary evaporation to dryness is avoided; on the other hand there is the necessity for a separate determination of carbonates and the difficulty of effectively washing the barium carbonate precipitate. The method would be useful in the case of cyanide samples containing ammonium salts, as it enables the cyanate to be determined without a separate determination of ammonium, such as would be necessary in such a case with Herting's method.

Criticism of the Method of E. Victor (see Chemistry of Cyanide Solutions, p. 106, Method No. 2).

Dr. Ewan (*Journal* Soc. Chem. Ind., March 15, 1904, p. 244) notes that silver cyanate is somewhat soluble in water, hence cyanates cannot be completely precipitated in neutral solution by silver nitrate. Moreover, silver cyanate dissolves somewhat slowly in cold 5 per cent nitric acid, whereas hot acid also dissolves some cyanide. It is therefore difficult to make sure of dissolving all the cyanate without dissolving some of the cyanide. An analysis made by Victor's method on a sample of sodium cyanate containing a little cyanide gave a result for the cyanate about 3.5 per cent too low as compared with Dr. Ewan's distillation method. The sources of error become of greater importance when the quantity of cyanate is small compared with that of cyanide, and in presence of hydroxides and some other substances giving silver salts soluble in nitric acid, the method was found to be incapable of giving even approximately accurate results. The presence of excess of silver nitrate diminishes the solubility of silver cyanate. According to Walker and Hambly (*Transactions* Chem. Soc., LXVII., 747) AgCNO is practically insoluble in water containing excess of $AgNO_3$.

Estimation of Cyanate by Alkalimetric Method.

The following extremely simple method is recommended by A. C. Cumming and Orme Masson (*Proceedings* of Soc. of Chem. Ind. of Victoria, July–August, 1903; see also *Chem. News*, January 5, 1906, p. 5). The method depends on the facts

(*a*) that cyanates are neutral to methyl orange

(*b*) that when boiled for a short time with a mineral acid they are quantitatively converted into CO_2 (which escapes), ammonium salts, and salts of the metal originally present in the cyanate, by the reaction

$$NaCNO + 2HCl + H_2O = NaCl + NH_4Cl + CO_2$$

or its analogues.

The method is as follows:

A known volume of the solution (which may contain carbonates as well as cyanides and cyanates) is first titrated in the cold with standard acid, using methyl orange or congo indicator. The quantity of acid required to affect a change in a neutral solution of the indicator should also be determined, and the proper correction applied in making the test. Having noted the point where the solution becomes neutral, a sufficient measured excess of standard acid is added beyond this point. The mixture is then boiled for a few minutes to insure the complete decomposition of cyanate and expel the CO_2. The boiling may be stopped when bumping sets in. The solution is then cooled and more indicator added if necessary. The residual excess of acid is now determined by titrating back with standard alkali. The difference between the excess acid added beyond the neutral point, and the residual acid is the equivalent of the cyanate, according to the equation given above.

As a check on the result, an independent measure of the cyanate may be obtained as follows: After the last-mentioned titration a sufficient excess of alkali is run in and the mixture is boiled until all ammonia has been expelled. The mixture is cooled, fresh indicator added if necessary, and the residual alkali titrated with standard acid. The difference between the amount of standard alkali added and the amount found is the equivalent of the cyanate, unless the original solution contained ammonium salts. In the latter case, the difference in the results obtained by the two methods of titration gives a means of estimating the ammonium present.

From the equation it is evident that in the first method 1 c.c. N/10 acid consumed = 0.0021 grams CNO, whereas by the second method 1 c.c. N/10 alkali consumed = 0.0042 grams CNO.

Let a = no. of c.c. of N/10 solution required by first method.

b = no. of cc. of N/10 solution required by second method.

Then $a \times 0.0021$ = gram CNO present.

$2\,b \times 0.0021$ = gram CNO when no ammonium is present, or $a = 2\,b$.

In presence of ammonium,

$(2\,b - a) \times 0.0009$ = gram NH_4 present.

Separation and Estimation of Cyanates, Cyanurates, Ammonium Salts and Urea.

C. J. Ellis ("Notes on Residual Cyanide Solutions," *Journal* Soc. Chem. Ind., February, 1897) gives the following, applicable in presence of cyanides, ferrocyanides, chlorides, etc.

To the solution, barium nitrate solution in slight excess is added to decompose the carbonates and cyanurates if present in moderate quantity. In presence of caustic alkali a very small excess of carbonic acid water is added to carbonate it before the addition of the barium solution. Barium carbonate and cyanurate are precipitated, leaving the other salts in solution. The liquid is filtered and silver nitrate solution run in, to slight excess. In neutral solutions the necessary quantity of $AgNO_3$ may be ascertained by using the chromate indicator. The precipitate consists of silver cyanide, ferrocyanide, thiocyanate, cyanate, chloride, etc. Of these only the *cyanate* is soluble in dilute nitric acid. The mixture is therefore shaken up with dilute nitric acid and filtered. The silver in the filtrate is titrated by Volhard's method and calculated to cyanic acid. (Comp. Text p. 106.)

Another portion of the original substance or solution is treated in precisely the same way, but substituting calcium nitrate for barium nitrate. Calcium cyanurate being soluble in water remains in the filtrate from the carbonate precipitate, and is precipitated by silver nitrate as a silver salt soluble in dilute nitric acid. The final titration of the dissolved silver therefore represents cyanate + *cyanurate.*

To the original filtrate from the precipitate of silver cyanide, ferrocyanide, etc., a little common salt is added to remove excess of silver. The silver chloride is filtered off and the filtrate distilled with a slight excess of KOH for a comparatively short time, keeping the liquid just barely boiling, the distillate being caught in a measured quantity of N/10 hydrochloric acid. The *ammonia* in the distillate is then determined by Nesslerizing or by titrating the residual acid.

If the distillation be carried out at a low enough temperature

and is not too prolonged, and if no great excess of potash be employed, little if any of the nitrogen of the *urea* pases over as ammonia with the distillate. The urea mostly remains undecomposed in the distilling flask, and may be determined by decomposing with hypobromite of soda and measuring the nitrogen evolved.

$$CO(NH_2)_2 + 3NaBrO = 3NaBr + 2H_2O + CO_2 + N_2$$

(See Sutton, *Volum. Anal.*, 8th ed., p. 432.)

The hypobromite solution is prepared by adding one-tenth of its volume of bromine to a 40 per cent caustic soda solution.

Estimation of Chlorides.

Method No. 6.

The following method was found by the writer to give satisfactory results in determining the amount of chloride in commercial cyanide. It is preferable to the differential methods (1, 2 and 3, pp. 109, 110) in cases where the amount of chloride is small compared with the amount of cyanide, and is much less troublesome than the methods involving a fusion with niter (4 and 5, p. 111). The results agree well with those obtained by other methods.

The cyanide is dissolved in water, with addition of ammonium nitrate or, preferably, ammonium sulphate, and heated to boiling for some time. The cyanogen is completely expelled as ammonium cyanide,

$$(NH_4)_2SO_4 + 2NaCy = 2NH_4Cy + Na_2SO_4$$

the chloride remaining unaffected. The liquid is then cooled, acidulated with nitric acid, a measured quantity of standard silver nitrate added, stirred and filtered. The excess of silver in the filtrate is determined by titration with standard thiocyanate and ferric indicator. The difference between the silver found and the silver added is the equivalent of the chloride.

APPENDIX. CLASS VI.

Estimation of Gold.

Comparison of Various Methods for the Estimation of Gold in Solutions.

G. W. Williams (*Journal* Chem. Met. & Min. Soc. of S. Africa, May, 1904) remarks as follows:

In assaying solutions by the "copper method" (*i.e.*, by Whitby's method: Chemistry of Cyanide Solutions, p. 117), the presence of ferrocyanide, shown by a brown precipitate of copper ferrocyanide, is advantageous. In assaying solutions free from ferrocyanide the results by the copper method were lower than by Crosse's silver method (Chemistry of Cyanide Solutions, p. 119). On adding ferrocyanide the results became equal. The effect of the ferrocyanide is entirely mechanical, the gelatinous precipitate acting as a very perfect filter, completely removing all other precipitates from solution.

The copper method gives results slightly lower than those obtained by evaporation or by Crosse's silver method, the error being least in presence of a good excess of ferrocyanide. By either the copper or the silver method it is possible, without exercising undue haste, to return an assay the accuracy of which is above suspicion within 2 or 3 hours, after making the most liberal allowances for cupellation and parting.

A. Whitby, however (*loc. cit.*, p. 54), maintains that the method gives higher results than either the evaporation or silver methods. He confirms the necessity of adding ferrocyanide and also adds sufficient cyanide to bring the strength up to 0.07 per cent KCy before proceeding with the test.

The present writer has frequently obtained results by the "copper method," both in its original form as communicated to him by Prof. S. B. Christy in 1898, and as modified by Whitby, which have agreed exactly with those obtained on the same solutions by evaporation, but solutions very low in gold values gave slightly lower results. For the "copper method" the following

quantities were used as a rule: 300 c.c. of solution to be tested, mixed first with 10 c.c. of 15 per cent copper sulphate, secondly with 10 c.c. of 25 per cent sodium bisulphite and finally with 5 c.c. of 10 per cent sulphuric acid, agitating after each addition and settling for 15 to 30 minutes before filtering. When necessary, small quantities of cyanide and ferrocyanide were added before making the test.

Modification of Durant's Method (p. 120).

N. S. Stines (*Min.* and *Sci. Press*, April 28, 1906) gives the following:

Take 100 c.c. of the solution to be assayed, add 7 c.c. of a 10 per cent lead acetate solution, then 1 gram of zinc shavings or dust, and place on a hot plate. Heat, but not to boiling, until the lead has gathered around the pieces of zinc. This usually takes about 25 minutes. This precipitation being complete, 20 c.c. concentrated HCl are added and the heating continued until all effervescence has stopped. The lead is then in such a spongy condition that by the aid of a flattened glass rod it can be pressed into a cake and the clear solution poured off. It is then washed twice and pressed with the fingers into a compact mass. This is dropped in a lead foil funnel, leaving a vent for escape of steam, placed on a hot cupel and the assay completed in the ordinary way. In order to keep the lead from breaking up, the solution should not be actually brought to a boil at any stage of the process.

Results with rich silver solutions were lower than by evaporation on lead foil.

S. J. Speak (*Transactions* Inst. Min. Met., XII, 389) mentions that Professor Liversidge, about 1895, used zinc shavings and lead acetate to precipitate gold in sea-water, probably in a slightly acid solution.

Precipitation of Gold from Cyanide Solutions by Means of Cement Copper.

Albert Arents (*Transactions* Amer. Inst. Min. Eng., February, 1903) describes the following:

250 c.c. of the solution to be tested are mixed with a few c.c. of sulphuric acid, agitated for several seconds, and then not less or much more than 1 grain of cement copper added. This is well boiled for about 10 minutes and filtered without washing.

One third of a crucible-charge of flux is then added to the filter containing the sediment and the paper folded over so that it may be readily removed. Another third of the charge is previously placed in the crucible; the filter with the flux is then transferred to the same, and the remaining third of the charge placed on the top. It is then fused and assayed in the ordinary way, using a crucible of size F, and 30 grams of litharge. The filter itself furnishes the reducing agent, about 20 grams of lead being obtained. The lead button comes out bright and clean, and upon cupelling furnishes a bead free from copper.

A solution of copper sulphate to which a few pieces of sheet aluminum are added may be used instead of cement copper. The liquid is boiled until all the copper has come down, any undissolved aluminum being added with the residue on the filter, and fluxed as above.

Precipitation of Gold and Silver by Means of Copper Sulphides.

The following method, suggested by Prof. S. B. Christy, is given in *Min. and Sci. Press,* April 11, 1903.

From 3 to 10 assay-tons of the solution (say 75 to 300 c.c.), according to its richness, are boiled and acidified strongly. After 2 or 3 minutes 20 c.c. of a 5 per cent solution of copper sulphate are added, and when this boils, a sufficient quantity of sodium or potassium sulphide to precipitate the whole of the copper, but leaving an excess of acid in the liquid. The boiling is continued for another minute, or until the evolution of H_2S ceases. The precipitate of copper sulphide carries down the gold and silver. Either H_2SO_4 or HCl may be used for acidifying. The precipitate is collected on an 11 c.m filter, any precipitate adhering to the vessel being collected and added to the main bulk. The filter paper is then folded up and placed in front of the muffle on a $2\frac{1}{2}$ inch scorifier, until the paper is consumed and the sulphur burnt off. Grain lead and a small amount of borax are then added and the whole scorified. 20 grams of lead will usually suffice. It is advisable to scorify the button until it is reduced to 8 or 9 grams. It is then poured, cleaned from slag and cupeled.

It is stated that by boiling a number of solutions simultaneously, 15 to 20 assays may be prepared for scorification in $\frac{3}{4}$ hour.

Precautions. An excess of alkali must be avoided; as soon as all the copper is thrown down, further addition of sodium sulphide gives a white precipitate of sulphur. This, however, cannot be seen unless the copper sulphide has settled somewhat.

If the solution be acidulated *after* the copper sulphide has been thrown down, the precipitation of gold and silver is incomplete unless an excessive amount of copper sulphate has been added.

Excessive amounts of copper sulphate should be avoided as they cause large losses on cupellation. 1 gram is usually sufficient and gives results checking closely with evaporation with litharge.

The results are too low when the amount of sodium sulphide added is insufficient to precipitate all the copper.

Precipitation with Ammoniacal Copper Salts and Sulphuric Acid.

M. Lindeman (*Engineering and Mining Journal*, July 7, 1904, Vol. LXXVIII., p. 5) gives the following:

10 assay-tons of the solution are heated strongly. Ammoniacal copper nitrate is then added until the solution shows a permanent blue color. Sulphuric acid is then carefully added in excess, the solution stirred and immediately filtered. The paper is folded and carbonized in a scorifier transferred to a crucible, fused and cupeled. The method checks very well with evaporation with litharge.

General Remarks on Copper Methods of Estimating Gold and Silver in Solutions.

Whitby's method, described in the text (p. 117) possesses the great advantage over all the foregoing methods, and indeed over almost every suggested method for assaying cyanide solutions, that the preliminary operations can be carried out entirely in the cold. The apparatus, time and attention required for boiling or heating the solutions are thus saved.

Electrolytic Method of Estimating Gold in Cyanide Solutions.

D. Clark (*Australian Mining Standard*, April 24, 1902) mentions

the following as having been in use at the Bairnsdale (Victoria) School and elsewhere in Australia. The gold is precipitated by electrolysis from a measured volume of the solution on lead-foil cathodes. The lead is scorified and sometimes cupeled straight-away. This method is of course merely an application of the Siemens-Halske process on a small scale.

The same writer criticizes the method of evaporation with litharge on the ground that large losses may occur on account of the solutions being saturated with chlorides and other salts.

A. M. Henderson (*Journal* Soc. Chem. Ind. [1905] p. 942) gives a similar method, the cathode consisting of a cylinder of lead foil notched at the base, and the anode being a rod of wrought iron, a 6-inch nail answering the purpose. The solutions are electrolyzed for 4 hours with a current of 0.06 to 1.2 ampère. The gas bubbles liberated inside the cathode cylinder cause an upward current of solution, inside the cylinder, and a downward current outside which passes through the notches at the bottom, thus securing sufficient circulation of the liquid. An excess of ammonia is added to prevent the formation of Prussian blue on the anode. 20 assays of 10 assay-tons each can be made simultaneously, and the precipitation is said to be very complete, solutions of 10 to 15 dwt. gold per ton and 0.03 to 0.25 per cent cyanide being reduced below 3 grains gold. The gold separates as a bright yellow deposit. When precipitation is complete, the cathode is washed in water, dried, rolled up, scorified with test lead and cupeled.

Colorimetric Methods for Estimation of Gold in Cyanide Solutions.

Various attempts have been made to adapt the well-known "Purple of Cassius" test for the estimation of gold in presence of cyanides. The test cannot of course be applied directly, and all such methods necessarily involve either the oxidation of the cyanogen compounds, or the previous separation of the gold from them.

We shall here describe the methods suggested by Henry R. Cassel and J. Moir.

(1) Cassel's Method.

(*Engineering and Mining Journal*, October 31, 1903, LXXVI., 661).

About 50 c.c. of an ordinary working cyanide solution containing gold is mixed with a small amount of potassium bromate, and concentrated sulphuric acid added until all effervescence ceases. The solution is then boiled thoroughly, and a few drops of hydrochloric acid and stannous chloride added. The purple color forms almost immediately.

The following equation is suggested:

$$2KAu(CN)_2 + 6KBrO_3 + 4H_2SO_4 = 4K_2SO_4 + 2AuBr + 4CO_2 + 2N_2 + 4H_2O + 3O_2.$$

Potassium chlorate may be substituted for potassium bromate, but requires longer boiling.

The following is recommended as the best method of applying the test:

A measured quantity of the cyanide solution to be tested (say about 10 c.c.) is put into a boiling-tube. About 0.5 grams of potassium bromate is next added and then pure concentrated H_2SO_4 gradually with shaking until the action starts; once started it will go on without the further addition of acid. When the action has ceased, add drop by drop, preferably from a dropping bottle, a saturated solution of stannous chloride, best prepared by dissolving metallic tin in hydrochloric acid, until the solution is just colorless. The purple color will now form and will be most intense after standing for about half a minute. If left standing too long more bromine may be freed and this spoils the color. It is not necessary to boil off the bromine before adding stannous chloride. It is stated that a complete test may be made in $2\frac{1}{2}$ minutes.

Delicacy of the Test. — By careful manipulations 1 grain of gold per ton can be detected. Solutions containing 1 dwt. per ton show a color which is easily visible against a white ground. [On 50 c.c. of solution taken for test? J.E.C.] Solutions too weak to give a color should first be concentrated by evaporation. If too concentrated they should be diluted, as a dark solution cannot be accurately judged.

Other Modes of Preparing the Solution for the Test. — Potassium chlorate and HCl act fairly well, but require a large amount of

boiling. Potassium chlorate and sulphuric acid have the same disadvantage. Aqua regia gives no color at all; the excess of acid cannot be got rid of without evaporating to dryness. The cyanide may be expelled by continued boiling with H_2SO_4 if the percentage be small; the color, however, does not show readily.

Good results are obtained by adding successively potassium bromide, sodium peroxide and finally sulphuric acid until neutral. On adding HCl and stannous chloride the purple color forms with great readiness. The oxidation takes place as follows:

$$KAu(CN)_2 + 6Na_2O_2 + 3KBr + 8H_2SO_4 = AuBr_3 + 6Na_2SO_4 + 2K_2SO_4 + 2CO_2 + N_2 + 8H_2O.$$

Another method is to add to the solution to be tested about one-third of its bulk of concentrated ammonia, then concentrated H_2SO_4 till neutral. The solution so prepared readily gives the Purple of Cassius reaction.

The present writer's experience of Cassel's method is that other substances frequently occur in working solutions which interfere with the test either by giving precipitates with stannous chloride or by affecting the color of the gold compound. Among such interfering substances may be mentioned ferrocyanides of zinc and copper, and selenium. In any case it is advisable to use for comparison measured quantities of a model solution of known gold contents, and containing other ingredients likely to occur in the solutions to be tested in approximately similar proportions, as the tint obtained with (for instance) a pure solution of gold chloride may be very different from that obtained with a cyanide solution of equal gold contents.

(2) Moir's Method.*

In this process the gold is precipitated and separated from the solution before applying the Purple of Cassius test.

100 c.c. of the cyanide solution to be tested are poured into a 300 c.c. evaporating basin and treated with 1 to 2 grams of sodium peroxide, boiling for 2 minutes to destroy the cyanide. The quantity of peroxide and time of boiling are varied according to the amount of free cyanide present. Next 2 drops of 10 per cent lead acetate are added, whereon, if sufficient peroxide has been used, a brown spot of PbO_2 forms and redissolves. The

(* *Proceedings* Chem. Met. and Min. Soc. of S. Africa, IV., 298).

basin is then removed from the flame and about 0.1 gram of aluminium powder is added. The mixture is vigorously stirred until hydrogen ceases to come off. If the aluminium be pure, no further heating is required. The aurocyanide is electrolyzed by the aluminium-lead couple, and finally a black precipitate is obtained consisting of lead and gold. The mixture is filtered through a small paper and the dish rinsed out on to it. The liquid, being very alkaline, filters easily. The filtrate is rejected. Next 10 c.c. of aqua regia are warmed till yellow and poured into the paper: the liquid passing through is collected in a test-tube, boiled and poured through the paper again. This is repeated until the filter paper is perfectly clean, whereon it is washed out with a small quantity of water. The yellow filtrate is then treated with strong stannous chloride solution added drop by drop until the yellow color has faded.

If the original cyanide solution contained over 0.5 dwt. of gold, the purplish-blue shade appears at once, but if only a few grains per ton were present the mixture must stand a few seconds. After half a minute the full intensity is attained and the comparison with the standards is made.

Method of Standardizing. — For exact work, the solution is poured into a cylinder exactly 1 inch in internal diameter and made up to a definite volume, say 15 c.c., with water. The purple color fades through oxidation on keeping, and therefore cannot be used for a standard. A permanent imitation of the shade can be made by adding copper sulphate solution to cobalt nitrate solution until the exact tint is obtained; the mixture is diluted for use and standardized by the result of the foregoing process applied to cyanide solutions of known gold content.

For the range between 0.5 and 2 dwt. per ton, the most convenient standard is an "indigo-prism," a triangular bottle which, when filled with the colored fluid prepared as described above presents a varying thickness of liquid and can be graduated empirically once for all so as to read directly in dwt. per ton. This is held horizontally and moved across the cylinder at the level of the gold-containing liquid until its color is matched, when the value is read off. Another method is to prepare a set of standard tubes differing (say) by 3 grains. For quantities under 10 grains per ton the comparison is best made by looking down the tubes.

Limit of Accuracy. — The lower limit (on 100 c.c. of solution tested) is about 2 grains per ton, but by taking 500 c.c. of the solution the limit is about 0.4 grain per ton (1 in 35 million). Strong solutions should be diluted to twice or four times the volume, anything over 3 dwt. per ton gives a nearly opaque solution. With practice it is easy to estimate 0.2 dwt. by eye alone. The process is said to be quite as accurate as a fire assay on 100 c.c.

Reactions. — The oxidation of the cyanide takes place as follows:

(*a*) $KCN + Na_2O_2 + 2H_2O = Na_2CO_3 + NH_3 + KOH.$

The reduction of the aurocyanide by the lead-aluminum couple is due to nascent hydrogen:

(*b*) $Al + 3NaOH = Al(ONa)_3 + 3H.$

(*c*) $H + KAuCy_2 + NaOH = NaCy + KCy + H_2O + Au.$

The lead acetate forms first lead peroxide and eventually sodium plumbate, thus:

(*d*) $Pb\bar{A}_2 + Na_2O_2 = PbO_2 + 2Na\bar{A}.$

(*e*) $PbO_2 + Na_2O_2 = Na_2PbO_3 + O.$

The latter is reduced by nascent hydrogen to metallic lead:

(*f*) $Na_2PbO_3 + 4H = Pb + 2NaOH + H_2O.$

The lead and gold are dissolved simultaneously by aqua regia as chlorides. The best mixture for aqua regia is 100 c.c. concentrated HNO_3, 300 c.c. concentrated HCl and 400 c.c. water. This only evolves chlorine on heating.

Modified Method. — As a substitute for sodium peroxide a solution may be used consisting of 30 per cent NaOH and 0.1 per cent litharge. 10 c.c. of this is boiled with 100 c.c. of the cyanide solution for 5 minutes, then Al is added and the rest of the process carried out as before. In this case the cyanide is destroyed by nascent hydrogen and by hydrolysis and rather more time is needed:

(*g*) $3KCN + 4Al + 9NaOH + 3H_2O = 3Al(ONa)_3 + Al(OK)_3 + 3CH_3NH_3.$

(*h*) $KCN + 2H_2O = NH_3 + HCO_2K.$

Precautions. — As a check against incomplete precipitation of the gold, the alkaline filtrate should be tested for cyanide, with $FeSO_4$ and HCl (this test, however, is valid only in absence of ferrocyanides).

Stannous chloride is best dissolved in dilute HCl; the trace of a stannic salt usually present is advantageous, but the solution is filtered until absolutely clear. A piece of metallic tin may be added to the bottle containing the stock solution to prevent oxidation.

APPENDIX. CLASS VIII.

Estimation of Calcium.

Estimation of Calcium by Titration of Oxalate and Permanganate

Method No. 1.*

The writer uses the following method, which appears to be accurate enough for technical purposes: 50 to 100 c.c. of the solution are acidified with 10 c.c. hydrochloric acid, boiled and filtered; the filtrate is made alkaline with ammonia, again heated to boiling, and filtered if any turbidity appears. It is then mixed with a boiling solution of ammonium oxalate, allowed to stand till clear (say half an hour or so), filtered and the precipitate washed with hot water and titrated with permanganate. For this purpose the precipitate, after washing free from oxalates, is returned to the flask in which it was originally precipitated, using a jet of hot water. Moisten paper and funnel with 10 c.c. of 25 per cent HCl and allow washings to run into the flask. Heat the liquid to boiling, dilute to 50 c.c. with distilled water; add 5 c.c. concentrated H_2SO_4; heat to about 70° C. and titrate with N/20 permanganate (1.5803 gram $KMnO_4$ per liter) of which 1 c.c. = 0.001 gram Ca = 0.001 per cent Ca on 100 c.c.

Method No. 2.

According to G. W. Williams (*Journ.* Chem. Met. and Min. Soc. S. Africa, May, 1904) precipitation by oxalate in boiling solutions gives results slightly too low. He therefore recommends the following:

Evaporate, say, 250 c.c. in a porcelain or platinum dish. In the former case transfer to a platinum dish at the finish. When nearly dry add a few c.c. of concentrated HCl. Evaporate to dryness, and heat residue to destroy all sulphocyanides. Add 5–10 grams of a mixture in equal parts of potassium and sodium

*See *Engineering and Mining Journal*, June 29, 1905.

carbonates, fuse 5 minutes, washing the dish well with the fused carbonates. Extract with water, filter and wash well. Boil residue with dilute acid, filter, precipitate iron with ammonia and filter off. To the boiling filtrate add ammonium oxalate. Allow to stand and determine calcium either gravimetrically, or by permanganate as in Method No. 1.

Estimation of Manganese.

* Estimation of Manganese by Colorimetric Method.

Manganese in cyanide solutions commonly exists in an unstable form which readily deposits brown hydrated oxide of manganese on standing. It may be readily estimated by acidifying a measured volume, say 100 c.c. of the solution, pretty strongly with 5 to 10 c.c. nitric acid, heating to boiling, adding peroxide of lead and again boiling. The mixture is then made up to a definite volume in a measuring flask, by addition of boiled distilled water, and after standing till it has settled quite clear, an aliquot part is drawn off, and the tint compared with that of a similar volume of water to which standard permanganate is added until the colors are alike. The manganese contents of the permanganate solution being known, the amount present in the liquid tested is easily calculated:

$$1 \text{ gram } KMnO_4 = 0.3476 \text{ gram Mn.}$$

The process may be hastened by filtering off a measured volume of the mixture, but if a paper filter be used, the first portions passing through, say 10 c.c., must be rejected.

A convenient standard solution contains 0.1435 grams $KMnO_4$ per liter or 1 c.c. = 0.00005 gram Mn.

Estimation of Zinc.

Estimation of Zinc by Ferrocyanide Method.

Of the numerous proposed methods, the writer has found the following to be the most generally serviceable. Take 50 to 100 c.c. of the solution to be tested. Make strongly alkaline with NaOH. Heat to boiling. Add sodium sulphide in slight excess. Allow to settle somewhat. Wash by decantation and finally on filter, with boiling water. Dissolve the precipitate in about 10 c.c. of HCl, boil and filter; dilute filtrate to 100 or 150 c.c. according to amount of zinc present, filter again if not quite clear, and heat

* See *Engineering and Mining Journal*, June 29, 1905.

to 70° or 80° C. Titrate with standard ferrocyanide and uranium indicator in the ordinary way. It is preferable to add an excess of ferrocyanide, say 2 c.c., beyond the amount required to give a distinct brown spot with the uranium indicator. After warming gently 10 minutes, the excess of ferrocyanide is titrated with a zinc chloride solution corresponding in strength with the ferrocyanide. The difference of the two titrations gives the equivalent of the zinc. A convenient strength for the standard solutions is 1 c.c. = 0.002 gram Zn.

The only metals likely to be present which would be precipitated as sulphides along with the zinc under these conditions are silver, lead and mercury. Silver is almost completely removed in the subsequent treatment with HCl and filtering; lead and mercury could be precipitated by adding a few drops of H_2SO_4 before the final filtration.

According to A. Whitby (*Journal* Chem. Met. and Min. Soc. of S. Africa, III., 15) 1 part $K_4FeCy_6 = 0.265$ parts Zn; it is, however, always preferable to standardize the ferrocyanide on a zinc solution of known strength.

Estimation of Zinc by Means of Mercuric Chloride Solution.

L. M. Green (*Min. Sci. Press.*, January 28, 1905) gives the following, depending on the reactions of mercuric chloride with cyanides and double cyanides of zinc in presence of ferrocyanides. To a solution of KCy and K_2ZnCy_4 add a large excess of K_4FeCy_6 and $NaHCO_3$. On titrating with mercuric chloride solution, when about two-thirds of the KCy has been taken up by the $HgCl_2$ (viz., when the $HgCy_2$ and KCy are in the proportion of $HgCy_2$: KCy), the further addition of mercuric chloride causes a white cloud of a ferrocyanide precipitate, which the author believes to be a double ferrocyanide of mercury and zinc.

For the process, two standard solutions are required:

(1) The ordinary standard $AgNO_3$ solution containing 13.04 grams per liter. 1 c.c. = 0.01 gram KCy.

(2) A solution of mercuric chloride containing 10.422 grams per liter. 1 c.c. = 0.005 gram KCy.

The following tests are made: —

(*A*) Take 10 c.c. of the solution to be examined, add a slight excess of NaOH and a little K_4FeCy_6 together with a few drops of a strong solution of KI. If ferrocyanide be not added the

result is apt to be slightly too high where much copper is present. Titrate with $AgNO_3$ solution till a permanent yellow cloudiness is formed, disregarding any whitish turbidity occurring previously. Result a c.c.

(*B*) Take 10 c.c. of the solution; add a large excess of K_4FeCy_6 and $NaHCO_3$. Titrate with $HgCl_2$ until a permanent milky cloud is formed. Towards the finish add the $HgCl_2$ 2 drops at a time, waiting about 20 seconds between each addition. Result b c.c.

By the first test, $a \times 0.01$ = grams KCy present as free cyanide and as zinc double cyanides, on 10 c.c. of the liquid tested; hence $\frac{a}{10}$ = per cent of "total cyanide" present.

By the second test, $b \times 0.005 = \frac{3}{4}$ of free KCy present in 10 c.c., or free KCy in 10 c.c. $= \frac{3}{4}\frac{b}{0}$ hence $\frac{3b}{40}$ = per cent of free KCy.

The difference between these amounts, *i.e.*, $\frac{a}{10} - \frac{3b}{40}$ or $\frac{4a - 3b}{40}$ = per cent KCy present as K_2ZnCy_4 and $\frac{1}{4}$ of this, or $\frac{4a - 3b}{160}$ is the percentage of zinc.

Estimation of Copper.

Colorimetric Method with Ammonia.

Copper may in most cases be rapidly estimated as follows: 100 c.c. of the solution are acidulated pretty strongly with HCl, heated to boiling, 0.5 gram potassium chlorate added, and boiled till most of the chlorous gases are expelled. The liquid is then made alkaline with ammonia and filtered. The tint of the filtrate is compared with that of a similar volume of water, to which HCl and ammonia have been added in about the quantities used in the test, and to which standard copper solution is added until the colors of the two liquids are alike. The standard copper solution is prepared as described in the text, p. 135, l. 2.

The above treatment with potassium chlorate is generally sufficient for the complete oxidation of all cyanogen compounds, but in a few cases it may be necessary to add a little bromine. When much ferrocyanide is present, however, the method No. 1, described in the text (p. 134), should be used.

INDEX

INDEX.

PAGE

Active cyanogen compounds..2, 4
Active haloids, estimation of... 100
Adair, Alfred, cited 76
Alkaline constituents..... 2, 58
action toward alkaline hydrates 59
action toward alkaline monocarbonates 59
action toward alkaline sulphides 60
action toward alkaline zincates 60
action toward ammonia..... 60
action toward bicarbonates.. 59
action toward simple cyanides 58
action toward zinc cyanides.. 60
Alkaline earths, estimation of. 137
Alkaline iodide indicator..... 10
Alkaline metals, estimation of. 137
Alkalis, test illustrating the influence of 11
Ammonia, estimation of..... 68
Ash, determination of..... 139
Auxiliary agents.....2, 95
Available cyanide, estimation of 54, 56
Base metals 2, 123
Bettel, W., cited..23, 30, 35, 53, 56, 68, 72, 103
Bicarbonates, estimation of.66, 67
Brown, E. O., cited..... 134
Carbonates, estimation of..66, 67
Chlorides, estimation of..... 108
tests illustrating the influence of 16
Christy, S. B., cited..... 116
Colorimetric method for estimation of sulphides..... 92
for estimation of thiocyanates 89
Copper, estimation of.....134, 135
Crosse, A. F., cited.....42, 65, 97, 99, 126
Cyanates and isocyanates, estimation of 104
Cyanide solutions, ingredients of 2

PAGE

Cyanogen bromide, estimation of 100
Cyanogen in compound cyanides, estimation of..... 42
Denigès, G., cited.....8, 9, 10
Durant, H. T., cited..... 120
Ellis, Charles J., cited....26, 36
Ferricyanides, estimation of, 102, 103
Ferrocyanides, estimation of, 73, 74, 75, 78, 79, 82, 83, 85
test illustrating the influence of 19
Free cyanide, estimation of, 4, 26, 28, 31, 32
Gasch, R., cited 83
Gasometric method for estimation of oxygen..... 96
Gold, estimation of....114, 118, 119, 120
Gold and silver, estimation of. 114
Goyder, G. A., cited....35, 36, 37
Gravimetric determination of total cyanogen 49
Green, L. M., cited..34, 49, 64, 132
Green's method 158
Haloids, active..... 100
Hannay, J. B., cited..... 31
Herting, O., cited.....107, 108
Hurter, F., cited..... 82
Hydrates, estimation of....66, 67
Hydrocyanic acid, estimation of 52, 53
Inactive bodies 2, 104
Iodine absorbents, tests for.... 98
Iron, estimation of..... 137
James, Alfred, cited..... 116
Knublauch, O., cited..... 80
Knublauch's method.....80, 81
Kraut, K., cited..... 11
Lead salts in estimation of sulphides 90, 91
Lenssen, E., cited..... 102
Leybold, W., cited..... 85
Liebig's method, or estimation of free cyanide 4, 78, 23
Loevy, J., cited..... 92
Longmaid, John, cited..... 33

PAGE
Maclaurin, J. S., cited..... 55
McArthur, J. T., cited.....8, 26
Mellor, J. W., cited.....107, 112
Müller, J., cited..... 83
Nitrates, estimation of....93, 112
Noble metals.....2, 114
Organic matter, estimation of. 72
Oxidizable organic matter, estimation of..... 72
Oxygen, estimation of..95, 96, 97
test for 98
Peroxides, estimation of..... 101
Protective alkali, definition of. 61
estimation of.....63, 64, 65
Reducing agents 2, 70
Reducing power, definition of. 72
estimation of..... 70
Rose, H., cited..... 51
Rose, T., Kirke, cited..... 24
Sharwood, W. J., cited..11, 24, 27, 35, 85, 113
Silicates, estimation of..... 113
Silver, estimation of.....114, 120
Sodium nitroprusside, preparation of 92
Sulphates, estimation of..... 112
Sulphides, estimation of..90, 92, 93
PAGE
Sulphocyanides (see thiocyanates).
Suspended matter 2, 138
Sutton, cited 53
Tcherniac, J., cited..... 75
Thiel, A., cited..... 88
Thiocyanates, estimation of..87, 89
tests illustrating the influence of 23
Thorpe, cited..... 77
Thresh's method for estimation of oxygen 97
Total alkali, definition of..... 61
estimation of..... 62
Total cyanide, estimation of, 33, 34, 37, 38, 39, 40
Total cyanogen, estimation of, 47, 48, 49
Total solids, estimation of..138, 139, 140, 143
Victor, E., cited..... 106
Vielhaber's method 48
Virgoe, W. H., cited..... 38
Watson, Henry, cited..... 118
Weith, cited..... 51
Whitby, cited 117
Zaloziecki, R., cited..... 84
Zinc, estimation of....123, 124, 125, 126, 127, 128

RETURN TO **ENGINEERING LIBRARY**

642-3366

LOAN PERIOD 1	2	3
4	5	6

ALL BOOKS MAY BE RECALLED AFTER 7 DAYS

Overdues subject to replacement charges

DUE AS STAMPED BELOW

JAN 12 1981

UNIVERSITY OF CALIFORNIA, BERKELEY

FORM NO. DD11, 80m, 8/80 BERKELEY, CA 94720

YC 33908

300326

Clennell

TN761
C59
1910
Mining
Dept.

UNIVERSITY OF CALIFORNIA LIBRARY